University of Alberta

Ancillary Ligand Effects in the Cobalt-mediated [5+2] Pentadienyl/Alkyne Cycloaddition Reactions

by

Andrew Douglas Kirk

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Master of Science

Department of Chemistry

Edmonton, Alberta
Fall 2007

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ISBN: 978-0-494-33281-8
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for Racqel and Caleb

Abstract

Cationic cyclopentadienylcobalt(η^5-pentadienyl) complexes undergo thermal cycloaddition reactions with various alkynes under mild conditions to yield novel η^5-cycloheptadienyl species. These systems are amenable to subsequent nucleophilic alkylation and oxidative demetallation to afford synthetically challenging seven-membered rings with complete control of stereochemistry and minimal control of regiochemistry. Initially developed using the (pentamethylcyclopentadienyl)cobalt systems, this investigation has established that simple cyclopentadienylcobalt(η^5-pentadienyl) complexes also mediate this potentially valuable transformation, offering a more convenient and cost-effective alternative. The reaction begins with readily available Nazarov-type 1,4 pentadien-3-ol precursors and either the cobalt(I) dicarbonyl or bis(ethylene) complex, which are converted in the presence of protic acid into the corresponding cationic η^5-pentadienyl complexes. The cycloaddition is effective for a range of alkynes, including acetylene itself. For some substrates, unusual, kinetically formed, η^3,η^2-cycloheptadienyl products are isolated, whereas in other cases the reaction proceeds through this intermediate to give the thermodynamically more stable η^5-cycloheptadienyl complexes.

Acknowledgements

I would first like to thank Christ Jesus who has given me the strength and endurance for the present research. I would also like to acknowledge the tireless support of my family, in particular my wife, Racqel, son, Caleb, sister-in-law, Roxy and parents and parents-in-law. Dr. Jeffrey Stryker has been a ready source of guidance and wisdom, and I would like to thank him for his mentoring and supervision. I have learned much from the Stryker group, and in particular, Team Cobalt (R. Witherell, K. Ylijoki and B. Chan). Special thanks to Dr. Masaki Morita for his patient assistance reading over the thesis manuscript(s) and providing invaluable feedback. In addition, I would like to extend appreciation to the staff of the X-ray crystallography labs (Dr. R. MacDonald, Dr. M. Ferguson), NMR labs (Dr. A. Otter, G. Bigam, L. Kong, M. Miskolzie, N. Dabral), mass spectrometry labs (Dr. R. Whittal, Dr. A. Morales-Izquierdo, D. Morgan, J. Zheng), and microanalysis labs (W. Moffat, R. Lister, M. Kaban) for their commitment to providing the highest quality support for structure characterization and identification available. As well, the laboratory would not be the same without the skilled services of our glassblowers (G. Streefkerk, T. Carter) or machinists (H. Hofmann, D. Starke, R. Lipiecki, R. Tomski, V. Bizon, R. Benson, P. Crothers).

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List of Abbreviations

Å	Angstrom(s)
AIBN	Azobisisobutyronitrile
AN	acetonitrile
APT	attached proton test
atm	atmospheres of pressure
calcd	calculated
COSY	Correlated Spectroscopy
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
CpH	cyclopentadiene monomer
deg.	degree(s)
Et	ethyl
equiv	equivalent
g	gram(s)
GCOSY	gradient COSY
H_a	allyl anti proton
H_c	allyl central proton
H_s	allyl syn proton
h	hour(s)
Hz	hertz
gHMBC	gradient heteronuclear multiple bond coherence
gHMQC	gradient heteronuclear multiple quantum coherence
gHSQC	gradient heteronuclear single quantum coherence
i	iso
IR	infrared
L	liter
M	metal
Me	methyl
mL	milliliter
MS	mass spectrometry

NMR	nuclear magnetic resonance
n	normal
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
Pr	propyl
R	alkyl group
t	tert
Tp	tris(pyrazolyl)borate
Tp*	tris(3,5-dimethylpyrazolyl)borate
TCNE	tetracyanoethylene
THF	tetrahydrofuran
TIPS	tri-isopropylsilyl
TMS	trimethylsilyl
µL	microliter

Chapter One: Introduction

The synthesis of complex molecules has been one of the primary aims of synthetic organic chemists for the past century, with the complexity of targets (natural and unnatural) attempted as well as the technology utilized becoming ever more sophisticated. Medium-sized rings are a prevalent motif in many of these compounds. Even so, medium-sized carbocycles of ring size greater than six continue to present a synthetic challenge for which novel and innovative solutions are required.

Recently, transition metal-mediated (stoichiometric and catalytic) cycloaddition reactions have provided access to such medium-sized rings with high stereo- and enantiocontrol under (often) mild conditions. Seven-membered rings in particular have been synthesized via [4+3], [5+2], [3+2+2], and [2+2+2+1] cycloaddition reactions. The scope and limitations of these reactions as well as their synthetic utility have been previously reviewed,[1,2,3] and will not be discussed in detail here. The [5+2] cycloaddition reaction is of interest for our present study due to the relatively few examples accomplished and their generally poor to moderate yields and limited scope.

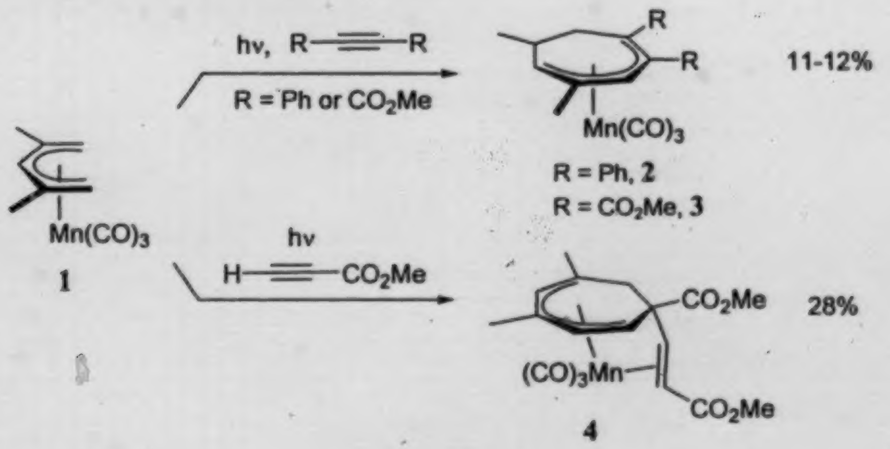
Metal-mediated [5+2] cycloaddition reactions can be achieved under both photochemical and thermal reaction conditions. Acyclic, or closed, pentadienyl ligands as well as cyclic, or open, ones have been used in these transformations. The discussion will begin with the development of photochemical [5+2] cycloaddition reactions, and continue with thermal [5+2] cycloaddition reactions.

---

[1] Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081.
[2] Dzwiniel, T. L. Ph.D. Thesis, University of Alberta, Edmonton, Alberta, Canada, 1999.
[3] Witherell, R. D. Ph.D. Thesis, University of Alberta, Edmonton, Alberta, Canada, 2007.

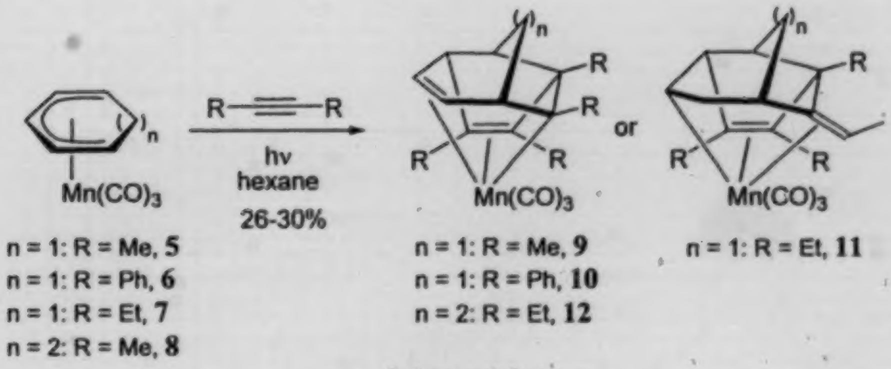
A. Photochemical [5+2] cycloaddition reactions

Manganese-mediated [5+2] cycloaddition of a pentadienyl ligand and an alkyne were developed independently by Kreiter, *et al.*[4, 5] and Sheridan, *et al.*[6] in the mid-1990's (Schemes 1.1-1.3). Both reported similar photochemical conditions; Sheridan, however, achieved better yields and higher regioselectivity.



hν, R—≡—R
R = Ph or CO2Me
Mn(CO)3
1
R
R
11-12%
Mn(CO)3
R = Ph, 2
R = CO2Me, 3
hν
H—≡—CO2Me
CO2Me
28%
(CO)3Mn
CO2Me
4

Scheme 1.1



Mn(CO)3
n
R—≡—R
hν
hexane
26-30%
n
R
R
R
R
Mn(CO)3
or
n
R
R
R
Mn(CO)3
n = 1: R = Me, 5
n = 1: R = Ph, 6
n = 1: R = Et, 7
n = 2: R = Me, 8
n = 1: R = Me, 9
n = 1: R = Ph, 10
n = 2: R = Et, 12
n = 1: R = Et, 11

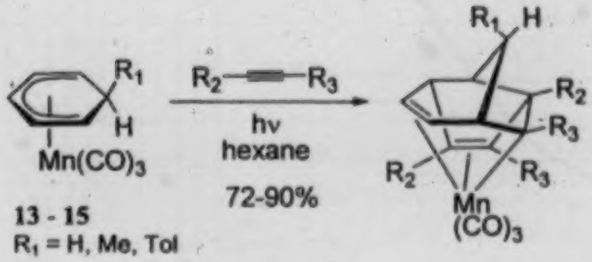
Scheme 1.2

---

[4] Kreiter, C. G.; Koch, E. C.; Frank, W.; Reiss, G. *Inorg. Chim. Acta* **1994**, *220*, 77.

[5] Kreiter, C. G.; Koch, E. C.; Frank, W.; Reiss, G. J. Z. *Naturforsch.* **1996**, *51*, 1473.

[6] Wang, C.; Sheridan, J. B.; Chung, H. J.; Cote, M. L.; Lalancette, R. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 8966.



13 - 15
R_1 = H, Me, Tol

	R_1	R_2	R_3
16	H	Me	Me
17	H	Ph	Ph
18	H	Et	Et
19	H	Me	Ph
20	Me	Ph	Ph
21	Tol	Me	Me

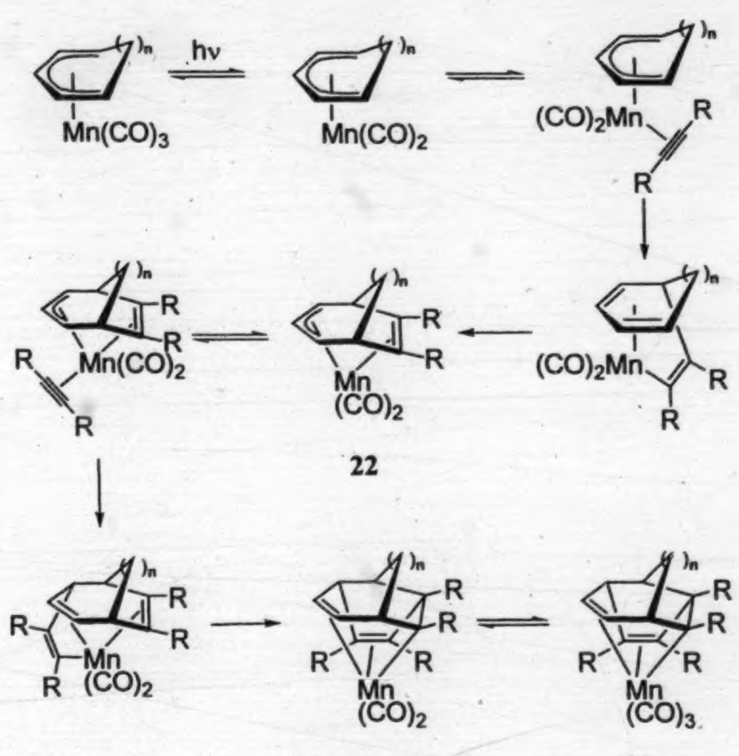
Scheme 1.3

Kreiter demonstrated that both open and closed pentadienyl ligands (**1** and **5 - 8**, respectively) participate in [5+2] cycloaddition reactions, albeit in low (12-28%) yields. Some cases, such as methyl proprionate, proceed with exclusively double alkyne addition (e.g. **4**); others, particularly with closed pentadienyl complexes, proceed with tandem [5+2] cycloaddition reactions, forming tricyclic products **9 - 12** (Scheme 1.2).[7]

Sheridan and Kreiter propose similar mechanisms for their cycloaddition reactions (Scheme 1.4). After photo-induced decarbonylation of manganese tricarbonyl complex, an alkyne is coordinated and then incorporated to form an allyl-olefin intermediate (**22**). For open pentadienyl ligands, the allyl-olefin intermediate spontaneously isomerizes to the fully conjugated cycloheptadienyl complex (cf., **2 - 4**). In the case of the closed pentadienyl ligands, another alkyne is coordinated and doubly inserted to form the tricyclic complex (**23**); isomerization is thwarted by the bridgehead in the case of the closed pentadienyl ligand.

---

[7] Kreiter, C. G.; Fiedler, C.; Frank, W.; Reiss, G. J. *Chem. Ber.* **1995**, *128*, 515.



Scheme 1.4

With closed pentadienyl ligands, Sheridan was able to arrest the tandem [5+2] cycloaddition reaction after single alkyne addition by limiting the amount of alkyne and purging with CO gas. The complex formed was the putative allyl-olefin intermediate (**22**) in moderate (16-39%) yields.[8] This is significant since, prior to Sheridan's work, only one example of a monocyclic η^3,η^2-cycloheptadienyl ligand had ever been claimed to have been isolated.[9] While Sheridan's isolation of the η^3,η^2 complex is significant, its synthetic utility is tempered by the structural constraints of the bridgehead, which prevents the possibility of isomerization. Recently, the Stryker group has reported the first examples of monocyclic Cp*- and CpCo(η^3,η^2-cycloheptadienyl) complexes that do not spontaneously isomerize to fully conjugated η^5-complexes.[10,11]

---

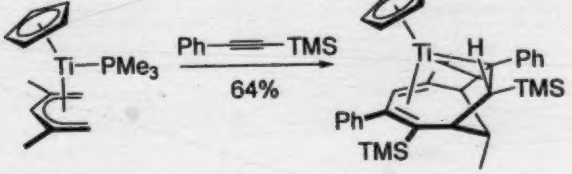
[8] Chung, H.-J.; Sheridan, J. B.; Cote, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 4575.

[9] Lewis, J.; Parkins, A. W. *J. Chem. Soc., A* **1969**, 953. In fact, it is unclear whether the compound reported was correctly identified, since the only characterization provided was an elemental analysis and low resolution NMR data.

While the photo-induced [5+2] cycloaddition reactions proceed relatively well (especially in the case of Sheridan), the reactivity is quite limited in scope (very limited range of substrates) and it is difficult to control the equivalents of alkynes incorporated. It has been necessary to look to different metal-mediated systems and different reaction conditions.

B. Thermal [5+2] cycloaddition reactions

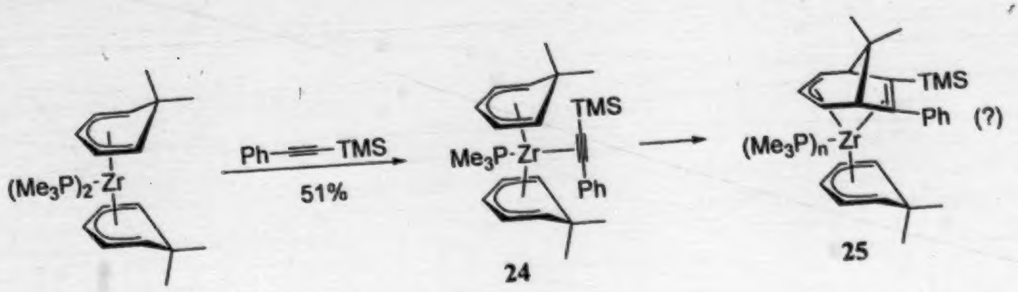
Historically, the first [5+2] cycloaddition reaction with pentadienyl ligands was achieved by Ernst in titanium[12,13,14] (Eq. **1.1**) and zirconium[14,15] (Scheme **1.5**). Closed pentadienyl ligands, for example, furnished bi- and tricyclic adducts via tandem [5+2] reactions. Ernst was also able to isolate pentadienyl-alkyne intermediate **24** and, after standing at room temperature in solution, a poorly characterized product purported to be the single alkyne adduct **25**. It is important to note that many of these cycloadducts were amenable to further cycloaddition reactions with the use of photo-irradiation.



Eq. 1.1

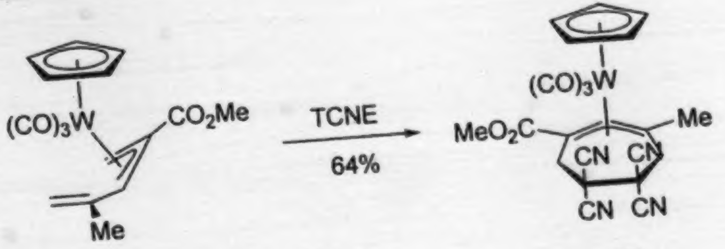
---

[10] Etkin, N.; Dzwiniel, T. L.; Schweibert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 9702.
[11] Witherell, R. D.; Ylijoki, K. E. O.; Stryker, J. M. Manuscript in preparation.
[12] Wilson, A. M.; Waldman, T. E.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 6252.
[13] Tomaszewski, R.; Hyla-Kryspin, I.; Mayne, C. L.; Arif, A. M.; Gleiter, R.; Ernst, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 2959.
[14] Harvey, B. G.; Mayne, C. L.; Arif, A. M.; Ernst, R. D. *J. Am. Chem. Soc.* **2005**, *127*, 16426.
[15] Basta, R.; Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta.* **2004**, *357*, 3883.


(Me$_3$P)$_2$-Zr
Ph—≡—TMS
51%
Me$_3$P-Zr
TMS
Ph
24
(Me$_3$P)$_n$-Zr
TMS
Ph (?)
25

Scheme 1.5

There are only two known examples of a metal-mediated [5+2] cycloaddition reaction with unsaturated species other than alkynes. The earlier report is an isolated example of the cycloaddition of a pentadienyl ligand with an electron-deficient olefin (Eq. **1.2**).[16] The tungsten-mediated process involves the cycloaddition of η^3-pentadienyl complex **26** with one equivalent of tetracyanoethylene to form η^3-cycloheptenyl complex **27**. The reaction is substrate specific and very limited in scope, yet it offered hope of future development of more general metal-mediated [5+2] pentadienyl/olefin cycloaddition reactions.


(CO)$_3$W
CO$_2$Me
Me
TCNE
64%
(CO)$_3$W
MeO$_2$C
Me
CN
CN
CN
CN

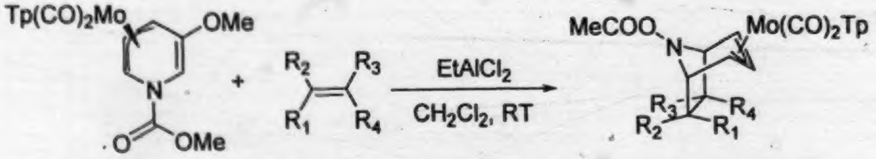
Eq. 1.2

26 **27**

The more recent example of a [5+2] pentadienyl/alkene cycloaddition reaction is the molybdenum-mediated work of Liebeskind, *et al*., in the enantioselective total synthesis of highly functionalized tropanes.[17] Unsaturated moieties (alkenes, allenes and alkynes) which were activated by electron-withdrawing groups react with a Tp(η^3-pyridinyl)molybdenum π-complex in good to excellent yield (47-88%) with good exo:endo selectivities (4 : 3 – 1 : 0) (Scheme **1.6**). Recently, Liebeskind and Zhang achieved the total synthesis of (-)-Bao Gong Teng A using the η^3-pyridinymolybdenum scaffold.[18]

---

[16] Yueh, T.-C.; Lush, S.-F.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1996**, *15*, 5669.



	R_1	R_2	R_3	R_4	% (endo : exo)
28	H	H	H	CO_2Me	88 (100 : 0)
29	H	H	Me	CO_2Me	47 (100 :0)
30	H	H	Me	CHO	74 (61 : 39)
31	H	-$(CH_2)_3$CO-		H	87 (100 : 0)
32	H	C-C bond		CO_2Me	68
33	=$CHCO_2Me$	CO_2Me		H	57

Scheme 1.6

In a different kind of [5+2] cycloaddition reaction, P. A. Wender, *et al.*, have joined vinyl cyclopropanes and various unsaturated two-carbon units (e.g. alkynes, alkenes, allenes, ketenes) using a catalytic rhodium system (Eq **1.3**).[19] The process is high yielding and can be achieved both inter- and intramolecularly on a broad range of substrates with short reaction times and low catalyst loading. As well, the process proceeds thermally to afford bi- and tricyclic systems enantioselectively when conducted in the presence of a chiral phosphine ligand.[20]

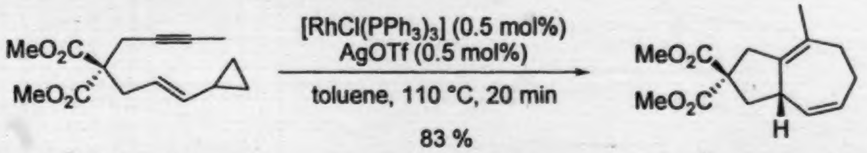
---

[17] Malinakova, H.C.; Liebeskind, L.S. *Org. Lett.* **2000**, *2*, 3909. Malinkova, H.C.; Liebeskind, L.S. *Org. Lett.* **2000**, *2*, 4083.

[18] Zhang, Y.; Liebeskind, L.S. *J. Am. Chem. Soc.* **2006**, *128*, 465.

[19] Wender, P. A.; Takahashi, H.; Witulski, B. *J. Am. Chem. Soc.* **1995**, *117*, 4720. Wender, P. A.; Sperandio, D. *J. Org. Chem.* **1998**, *63*, 4164; Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A.; Pleuss, N. *Tetrahedron* **1998**, *54*, 7203; Wender, P. A.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1940; Wender, P. A.; Rieck, H.; Fuji, M. *J. Am. Chem. Soc.* **1998**, *120*, 10976; Wender, P. A.; Fuji, M.; Husfeld, C. O.; Love, J. A. *Org. Lett.* **1999**, *1*, 137; Wender, P. A.; Glorius, F.;

One of the major drawbacks of this system, however, is the cost and toxicity of rhodium, even when used at catalytic scale. More importantly, though, is the synthetic cost of the organic substrate itself (e.g. the vinyl cyclopropane). Wender's [5+2] cycloaddition reaction can be achieved thermally, but due in large part to the energy imbued in the strained cyclopropane ring. Trost, *et al.*, have demonstrated similar reactivity using ruthenium catalysts.[21]



Eq 1.3

The Stryker group has demonstrated that Ru, Ir and Co mediate thermal cycloaddition reactions to afford seven-membered rings. The reactions proceed either via [3+2+2] cycloaddition of an allyl ligand with two alkynes or, more recently, [5+2]

Husfeld, C.O.; Langkopf, E.; Love, J.A. *J. Am. Chem. Soc.* **1999**, *121*, 5348; Wender, P.A.; Dyckman, A.J. *Org. Lett.* **1999**, *1*, 2089; Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Kadereit, D.; Love, J. A.; Rieck, H. *J. Am. Chem. Soc.* **1999**, *121*, 10442; Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Scanio, M. J. *Org. Lett.* **2000**, *2*, 1609; Wender, P. A.; Zhang, L. *Org. Lett.* **2000**, *2*, 2323. Wender, P. A.; Barzilay, C. M.; Dyckman, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 179; Wender, P. A.; Bi, F. C.; Brodney, M. A.; Gosselin, F. *Org. Lett.* **2001**, *3*, 2105; Wender, P. A.; Gamber, G. G.; Scanio, M. J. C. *Angew. Chem. Int. Ed.* **2001**, *40*, 3895; Wender, P. A.; Williams, T. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4550. Yu, Z.-X.; Wender, P. A.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 9154; Wegner, H. A.; de Meijere, A.; Wender, P. A. *J. Am. Chem. Soc.* **2005**, *127*, 6530; Wender, P. A.; Haustedt, L. O.; Lim, J.; Love, J. A.; Williams, T. J.; Yoon, J.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 6302.

[20] Wender, P. A.; Haustedt, L. O.; Lim, J.; Love, J. A.; Williams, T. J.; Yoon, J.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 6302.

[21] Trost, B. M.; Toste, F. D.; Shen, H. *J. Am. Chem. Soc.* **2000**, *122*, 2379; Trost, B. M.; Shen, H. C. *Org. Lett.* **2000**, *2*, 2523; Trost, B. M.; Shen, H. C. *Angew. Chem. Int. Ed.* 2001, 40, 2313; Trost, B. M.; Shen, H. C.; Schulz, T.; Koradin, C.; Schirok, H. *Org. Lett.* 2003, 5, 4149; Trost, B. M.; Shen H. C.; Horne, D. B.; Toste, F.D.; Steinmetz, B.G.; Koradin, C. *Chem. Eur. J.* 2005, 11, 2577.

cycloaddition of a pentadienyl ligand with an alkyne. These cycloaddition reactions will be discussed in further detail in Chapter Four.

The goal of the present research is to probe the effect of an isoelectronic but sterically less-hindered ancillary cyclopentadienyl ligand on the cobalt-mediated [5+2] cycloaddition reaction. The synthesis of cationic cyclopentadienylcobalt(III) pentadienyl complexes was developed, starting from readily available Nazarov-type pentadienol precursors and either cobalt(I) bis-ethylene or dicarbonyl complexes in the presence of a protic acid. The reactivity of these pentadienyl complexes toward [5+2] cycloaddition reactions with alkynes was then explored with special attention given to substrate scope and regioselectivity.

Chapter Two: Cyclopentadienylcobalt(ethylene)$_2$ and the synthesis of cobalt η^5-pentadienyl complexes

I. Background

A. Synthesis and use of CpCo(C$_2$H$_4$)$_2$ (34)

The organometallic chemistry of cobalt has been greatly impacted by the reactivity of the dicarbonyl and bis(alkene) complexes of cyclopentadienyl cobalt(I). CpCo(CO)$_2$ **(35)** has been found to be effective for numerous catalytic processes; the dicarbonyl complex and its use in the synthesis of η^5-pentadienyl complexes will be discussed in more detail in Chapter Three.

Bis(alkene) complexes were developed to provide even higher reactivity than the dicarbonyl analogues towards unsaturated organic molecules, due to the hemilability of the alkene ligands. Reactions with the bis(alkene) complexes can be achieved under low temperature conditions and without photo-irradiation. The alkene ligands are less π-acidic than carbonyl ligands, and, since they have lower back-bonding to the metal centre, they are more labile than carbonyl ligands.[22] Thus, CpCo(alkene)$_2$ complexes have found wide application in recent synthetic developments of the organometallic chemistry of cobalt (Scheme **2.1**).[23,24,25]

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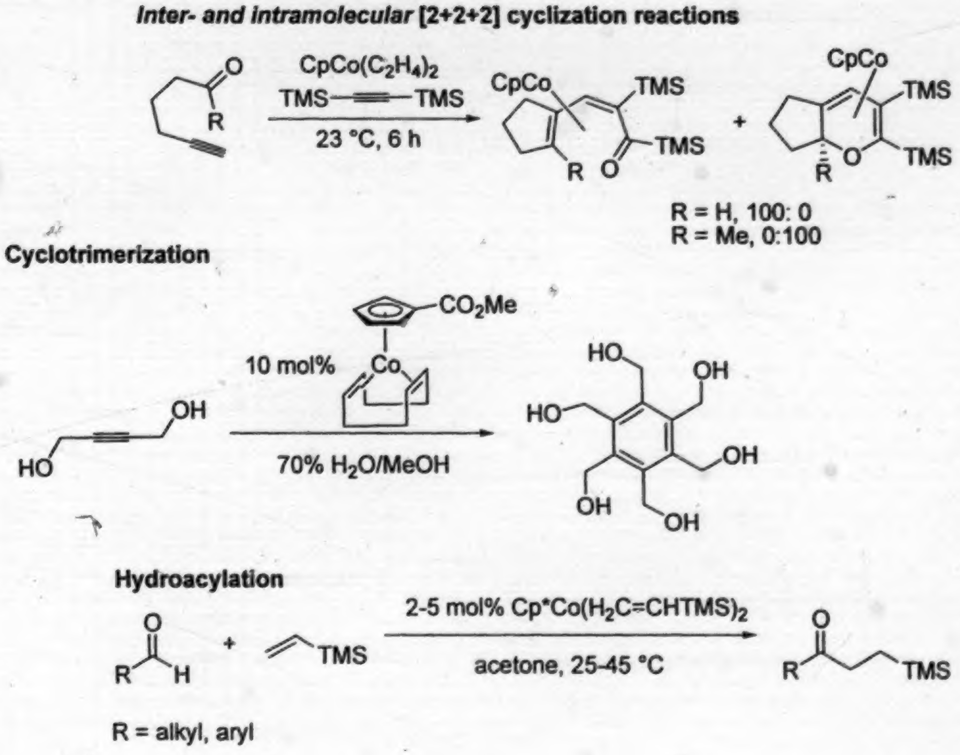
[22] Crabtree, Robert H. *The Organometallic Chemistry of Transition Metals.* 4th ed, Hoboken, NJ: John Wiley and Sons, 2005, pp.87ff [CO], 125ff [alkenes].

[23] [*Inter*- and *intra*molecular [2+2+2] Cyclizations]: Harvey, D. F.; Johnson, B. M.; Ung, C. S.; Vollhardt, K. P. C. *Synlett* **1989**, 15.

[24] [Cyclotrimerization]: Sigman, M. S.; Fatland, A. W.; Eaton, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 5130.

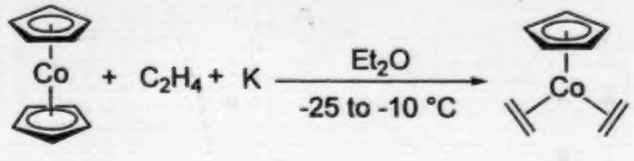
[25] [Hydroacylation]: Lenges, C. P; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 3165; Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6965.


Inter- and intramolecular [2+2+2] cyclization reactions
CpCo(C2H4)2
TMS—≡—TMS
23 °C, 6 h
CpCo
TMS
TMS
R
O
CpCo
TMS
TMS
R
O
+
R = H, 100: 0
R = Me, 0:100
Cyclotrimerization
CO2Me
Co
10 mol%
70% H2O/MeOH
HO
OH
Hydroacylation
2-5 mol% Cp*Co(H2C=CHTMS)2
acetone, 25-45 °C
R
H
TMS
R = alkyl, aryl

Scheme 2.1

$CpCo(C_2H_4)_2$ (**34**) offers practical advantages over dicarbonyl **35**, not the least of which is its ease of use. Complex **34** is a crystalline solid that can be weighed easily and accurately as well as purified by recrystallization. The greater reactivity, however, does not come without a cost; complex **34** is temperature-sensitive, decomposing slowly above -20 °C, especially in solution.

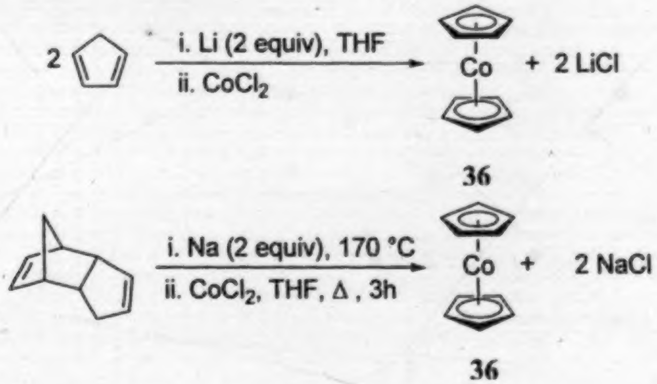
Since complex **34** is not commercially available, there are two well-established synthetic routes for large-scale preparation. The procedures, however, are quite delicate (very sensitive to temperature and air), hazardous (e.g., potassium sand and/or mercury amalgam), and require careful Schlenk techniques. The most well-known synthesis of complex **34** was achieved by Klaus Jonas, *et al.* (Eq. **2.1**).[26]



Eq. 2.1

36 **34**

The advantage of the Jonas procedure is its brevity and simplicity. Although the 19-electron Cp_2Co (**36**) (a black crystalline material) is highly air-sensitive, it is easily synthesized from cobalt dichloride (anhydrous), cyclopentadiene and either lithium or sodium[27] (Scheme **2.2**), and can be purified by recrystallization (pentane) or sublimation (40 °C / 10^{-3} torr).[28] For the Jonas synthesis, the potassium must be handled with care and the reaction conditions can not rise above -10 °C to avoid the decomposition of the product (Eq **2.1**). The orange-brown needles of **34** can be purified by recrystallization or sublimation (same conditions as **36**).



36

36

Scheme 2.2

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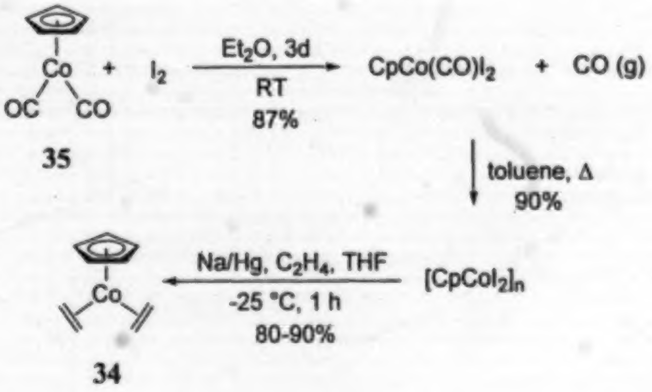
[26] Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520.
[27] Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2003**, *22*, 877.
[28] Bönnemann, H.; Bogdanovic, B.; Brinkmann, R.; Spliethoff, B.; He, D.-W. *J. Organomet. Chem.* **1993**, *451*, 23-31. Wilkinson, G.; Pauson, P. L.; Cotton, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1970.

Beevor, *et al.*, had developed an alternative method with a milder and potentially safer reductant than potassium (Scheme 2.3).[29,30,31] The appeal of Beevor's method is the robustness of the intermediates – their ease of use and stability towards bench-top manipulations. Dicarbonyl complex **35**, the starting material for Beevor's synthetic route, can either be purchased or synthesized (see Chapter Three). The two decarbonylation reactions proceed in high yields (87%, 90%) and require only simple purification. Only the sodium amalgam reaction requires care for air-, moisture-and temperature-sensitivity and the reaction proceeds in high yield, 80-90%.



Scheme 2.3

B. η^5-Pentadienyl complexes of Co(III)

Based on the known reactivity of $CpCo(alkene)_2$ complexes, it is easy to imagine two synthetic routes to CpCo(III) pentadienyl complexes from complex **34** (Scheme **2.4**).

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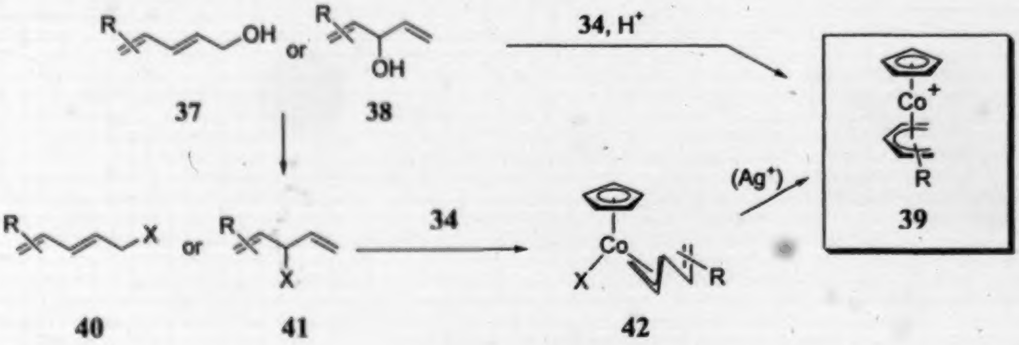
[29] $[CpCo(CO)I_2]$: Heck, R. F. *Inorg. Chem.* **1965**, *4*, 855. King, R. B. *Inorg. Chem.* **1966**, *5*, 82.
[30] $[\{CpCoI_2\}_n]$: Roe, D. M.; Maitlis, P. M. *J. Chem. Soc. A.* **1971**, 3173.
[31] $[CpCo(C_2H_4)_2]$: Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, *221*, C25.

The first option involves exchange of the ethylene ligands with the alkene moieties of a 2,4-pentadien-1-ol (e.g., **37**) or a 1,4-pentadien-3-ol (e.g., **38**) and loss of water by protonation, resulting in the formation of a cationic Co(III) η^5-pentadienyl complex (71). The second option is the oxidative addition of a pentadienyl halide (**41**) and the formation of a CpCo(η^3-pentadienyl) halide intermediate (**42**). Ionization of the halide, possibly with the assistance of silver(I), will isomerize the allyl and coordinate the pendant olefin to give the η^5-pentadienyl complex.



Scheme 2.4

There is a great deal of literature on the synthesis and reactivity of the pentadienyl ligand; we will not replicate such a survey here.[32] According to Kemmitt, organometallic pentadienyl complexes were relatively rare before the late seventies.[33] Since then there has been an explosion in synthetic scope and use in such areas as carbon-carbon bond activation (Spencer), nucleophilic addition to dienyl ligands (Bleeke), and cycloaddition chemistry (Kreiter, Sheridan, Ernst, Liu, Stryker), as discussed below.

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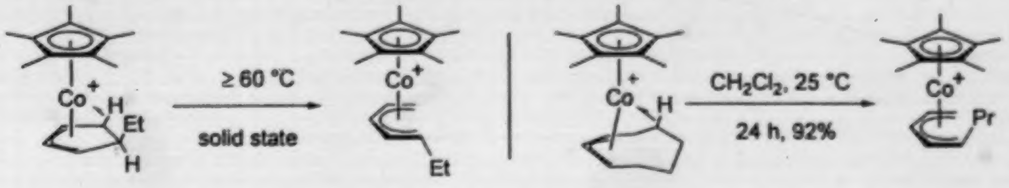
[32] Ernst, R. D. *Comm. Inorg. Chem.* **1999**, *21*, 285.
[33] Kemmitt, R. D. W. *J. Organomet. Chem.* **1981**, *211*, 279 (see p.358)

The organometallic chemistry of the pentadienyl ligand utilizes the versatility of the ligand and its ability to isomerize within a reaction manifold. Three distinct binding modes, in fact, have been assumed to be involved in the synthetic route postulated in Scheme **2.4**, as discussed in more detail below. The pentadienyl ligand has been reported to adopt η^1-, η^3- and η^5-coordination modes. Most η^5-pentadienyl ligands are U-shaped, although the S-shaped configuration has been reported in certain cases.[34]

Metal η^5-pentadienyl complexes have been synthesized from Group 4 (Ti, Zr), Group 8 (Mn, Re), and Group 9 (Co) metals. In the case of cobalt, only two research groups have reported the synthesis of η^5-pentadienyl complexes. Spencer, *et al.*, have prepared [Cp*Co(1-ethyl)pentadienyl]$^+$ (**44**) from the Cp*Co(η^3-cyclopentenyl) complex **43** via thermal metal-mediated carbon-carbon bond activation (Scheme 2.5).[35] Later, Spencer accomplished the preparation of the *endo* isomer of cationic Cp*Co(*n*-propylpentadienyl) complex (**46**), also by carbon-carbon bond activation.[36]



43 **44** **45** **46**

Scheme 2.5

Most of the known Co(III) η^5-pentadienyl complexes, however, have been synthesized by R. D. Witherell and K. E. O. Ylijoki in the Stryker group.[11] Using

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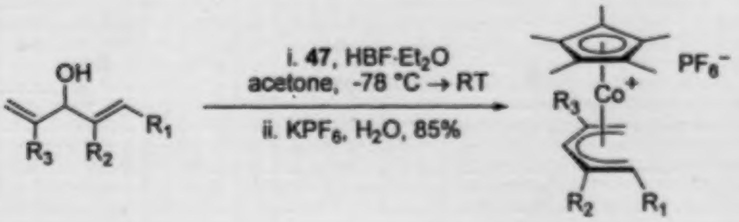
[34] For a more detailed treatment of the pentadienyl ligand, see ref. **3**.

[35] Bennett, M. A.; Nicolls, J. C.; Rahman, A. K. F.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328; Nicolls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781.

[36] Cracknell, R. B.; Nicolls, J. C.; Spencer, J. L. *Organometallics* **1996**, *15*, 446.

$Cp^*Co(C_2H_4)_2$ (**47**) and a variety of substituted 1,4-pentadienols in the presence of $HBF_4{\cdot}Et_2O$, Witherell assembled a modest range of $Cp^*Co(\eta^5$-pentadienyl) complexes **48** - **51** for further use in [5+2] cycloaddition reactions (Scheme **2.6**). Ylijoki synthesized $[Cp^*Co(1\text{-phenylpentadienyl})]^+BF_4^-$ and a variety of $Cp^*Co(\eta^5$-pentadienyl) complexes with tethered pro-nucleophiles for bi- and tricyclic ring formation, research currently in progress.



	R_1	R_2	R_3
48	H	H	H
49	Me	H	H
50	H	Me	H
51	Me	Me	H
52	Me	Me	Me

Scheme 2.6

II. Results and Discussion

The first step in the synthesis of $CpCo(\eta^5$-pentadienyl) complexes is the synthesis of the $CpCo(C_2H_4)_2$ (**34**). A recent modification of the Jonas preparation was employed.[37] While Jonas allows the reaction mixture containing **34** to reach -10 °C, Vollhardt maintains strict temperature control at -20 °C or below throughout the entire procedure (reaction – purification – sublimation).

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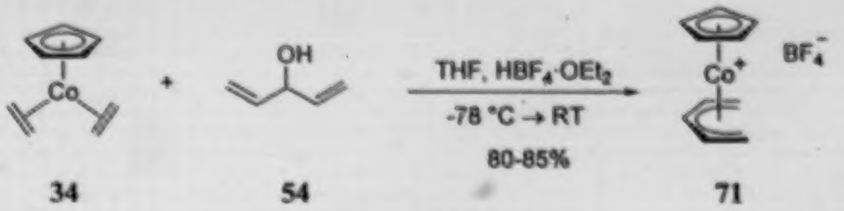
[37] Cammack, J. K.; Jalisatgi, S.; Metzger, A. J.; Negron, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1996**, *61*, 4798.

A. Pentadienyl complex synthesis: optimized conditions



Scheme 2.7

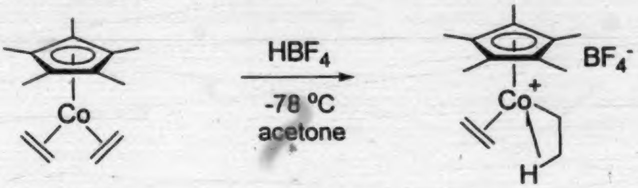
The synthesis of CpCo(η^5-pentadienyl) complexes then proceeded from the commercially available, unsubstituted 1,4-pentadien-3-ol (**54**) and bis-ethylene complex **34**. Initial reaction conditions (Scheme 2.7) were similar to those used for the Cp* ligand system. THF and HBF$_4$·Et$_2$O afforded the cationic CpCo(η^5-pentadienyl) complex **71** in good yield. The optimization of the reaction conditions for the cyclopendienyl series required varying the solvent, temperature, and the order of addition (Table 2.1).

Table 2.1. Optimization for the complexation of **34** and **54**

	Solvent	Temperature	Order of addition[a]	Yield (%)
A	THF	-78 °C → RT	I	low %
B	Acetone	-78 °C → RT	I	dec.
C	CH$_2$Cl$_2$	-78 °C → RT	I	dec.
D	THF	-78 °C → RT	II	70-80%
E	Acetone	-78 °C → RT	II	dec.
F	CH$_2$Cl$_2$	-78 °C → RT	II	dec.
G	THF	i) -78 °C → 0 °C; ii) -78 °C → RT	III	80-85%

[a] (I) HBF$_4$·EtO$_2$ was added to a solution of **1** at -78 °C and stirred for 15 min, followed by the addition of pentadienol **54**; (II) Pentadienol **54** was added to a solution of **1** at -78 °C and stirred for 15 min, followed by the addition of HBF$_4$·EtO$_2$ (1 equiv); (III) Pentadienol **54** was added to a solution of **1** at -78 °C, warmed to 0 °C and stirred for 15 min, followed by cooling to -78 °C and the addition of HBF$_4$·EtO$_2$ (1 equiv).

It is known that Cp*Co(ethylene)$_2$ is activated upon protonation at low temperature to give the agostic ethylene complex **53** (Scheme **2.8**).[11,38] Therefore, it was no surprise that Ylijoki observed that the yields for the synthesis of Cp*Co (η^5-pentadienyl) complexes from pentadienols with tethered pro-nucleophiles was significantly increased by adding acid to the bis(ethylene) complex prior to the addition of alcohol. It is reasonable to assume that the protonated bis(ethylene) complex is rendered more reactive toward alkene exchange with the pentadienol alkenes. Interestingly, Witherell observed that the order of addition had little impact on the yield of Cp*Co (η^5-pentadienyl) complexes from simple pentadienol substrates.



47 **53**

Scheme 2.8

In the case of the Cp ligand system, the order of addition of the acid and alcohol has a significant effect on the conversion achieved. Optimal conditions were obtained when the alcohol was added prior to the acid.

In the case of Cp*, the ancillary ligand increases the electron density on the metal and makes the metal more basic and reactive towards protonation. The cyclopentadienyl ancillary ligand, however, is less electron rich than Cp*, and therefore, the cobalt is less basic. The protonation of the cobalt center and the subsequent protonation of the organic substrate is thus in competition. Since the pentadienol substrates are very acid sensitive,

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[38] Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691.

the yield is likely lower in the case of initial acid addition by the formation of the expected Nazarov-type cyclization and other metal-free reaction pathways of the pentadienol substrates. Conversely, when the alcohol is added first and allowed to exchange with the more weakly-bound ethylene ligands of CpCo(ethylene)$_2$, the yields are increased.

The effects of reaction concentration were also briefly examined (17 mM, 34 mM, 85 mM of **34** in THF). Lower concentrations resulted in lower yields. Optimal conditions were obtained with 57 mM, nearing the upper limit of starting complex solubility.

B. Synthesis of alkyl-substituted η^5-pentadienyl complexes

Prior to synthesizing a variety of alkyl-substituted η^5-pentadienyl complexes, the synthesis of the organic substrates was required. The synthesis of many of the dienols was achieved by the simple addition of a Grignard or organolithium compound to an α, β-unsaturated aldehyde (enal) (Schemes **2.9**, **2.10**, **2.12**, Eqs. **2.2** – **2.4**). Due to the wide availability of Grignard reagents, a number of variably substituted dienols were easily assembled. Alternative synthetic methods were employed where the necessary organomagnesium or –lithium reagents were unavailable (Scheme **2.11**, **2.13**, **2.14**). The following compounds were synthesized from literature procedures: 1,4-hexadien-3-ol (**55**),[39,40,41] 1-phenyl-1,4-pentadien-3-ol (**56**),[42] 1-trimethylsilyl-1,4-pentadien-3-ol (**57**),[43,44] 5-methyl-1,4-hexadien-3-ol (**58**),[41,42,45,46] 4-methyl-1,4-hexadien-3-ol (**59**),[47] 2-

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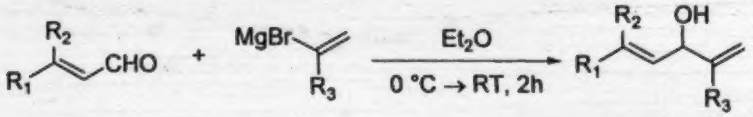
[39] Underiner, T. L.; Goering, H. L. *J. Org. Chem.* **1991**, *56*, 2563.
[40] Boccara, N.; Maitte, P. *Bull. Soc. Chim. Fr.* **1972**, 1448.
[41] Oppolzer, W.; Snowden, R. L.; Simmons, D. P. *Helv. Chim. Acta.* **1981**, *64*, 2002.
[42] Bertus, P.; Drouin, L.; Laroche, C.; Szymoniak, J. *Tetrahedron* **2004**, *60*, 1375.
[43] [via TMS-CH2CH2-SPh]: Hsiao, C-N.; Shechter, H. *Tetrahedron Letters* **1982**, *23*, 1963; Hsiao, C-N.; Shechter, H. *Tetrahedron Letters* **1983**, *24*, 2371.

methyl-1,4-hexadien-3-ol (**60**),[39] 2,5-heptadien-4-ol (**61**),[41] 2-methyl-1,4-pentadien-3-ol (**62**),[41] 3-methyl-1,4-pentadien-3-ol (**63**),[48] 3, 4, 5-trimethyl-2,5-heptadien-4-ol (**69**),[49] 1-cyclohex-1-en-1-ylprop-2-en-1-ol (**65**),[50,51,52] 1-(2-furyl)prop-2-en-1-ol (**66**),[53] 1-(3-furyl)prop-2-en-1-ol (**67**),[54] and 1-(3,4-dihydro-2*H*-pyran-6-yl)prop-2-en-1-ol (**68**).[55] 1-Cyclopent-1-en-1-ylprop-2-en-1-ol (**64**) was prepared by low temperature addition of 1-cyclopent-1-en-1-yl-magnesium bromide[56] and acrolein and subsequent distillation at reduced pressure.[57] 1-Trimethylsilyl-1,4-hexadien-3-ol (**70**), a new pentadienol, was synthesized using procedures analogous to the preparation of **57**.



R_1 = Me, R_2, R_3 = H, **55**, 62%
R_1 = Ph, R_2, R_3 = H, **56**, 89%
R_1, R_2 = Me, R_3 = H, **58**, 70%
R_1, R_2 = H, R_3 = Me, **62**, 79%
R_1, R_3 = Me, R_2 = H, **60**, unreported

Scheme 2.9

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[44] [via $SnBu_3$]: Baldwin, J. E.; Adlington, R. M.; Godfrey, C. R. A.; Patel, V. K. *Tetrahedron* **1993**, *49*, 7837.

[45] [MnO_2 synthesis of the 3-methylbut-2-enal]: Shaabani, A.; Mirzaei, P.; Naderi, S.; Lee, D. G. *Tetrahedron* **2004**, *60*, 11415.

[46] [PDC synthesis of the 3-methylbut-2-enal]: Corey, E. J.; Schmidt, G. *Tetrahedron Letters* **1979**, *5*, 399.

[47] Sample provided by R. Witherell (and previously from Dr. F. G. West and Dr. G. Murphy).

[48] Shing, T. K. M.; Zhu, X. Y.; Yeung, Y. Y. *Chem. Eur. J.* **2003**, *9*, 5489.

[49] Sample provided by J. Gauthier.

[50] Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta.* **1983**, *66*, 2377.

[51] [General Shapiro procedure]: Browder, C. C.; Marmsäter, F. P.; West, F. G. *Org. Lett.* **2001**, *3*, 3033.

[52] [Hydrazone synthesis]: Cusack, N. J.; Reese, C. B.; Risius, A. C.; Roozpeika, B. *Tetrahedron* **1976**, *32*, 2157; Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.

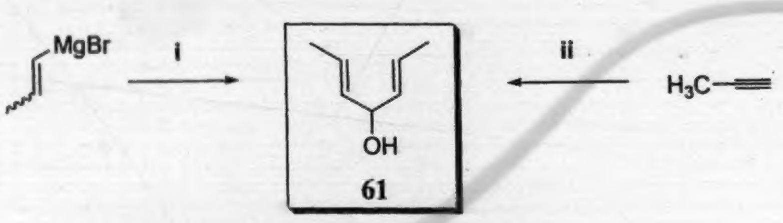
[53] Kusakabe, M.; Kitano, Y.; Kobayashi, Y.; Sato, F. *J. Org. Chem.* **1989**, *54*, 2085; Servi, S.; Topaloglu, C. *Molecules* **2004**, *9*, 22.

[54] Ito, M.; Kitahara, S.; Ikariya, T. *J. Am. Chem. Soc.* **2005**, *127*, 6172; Gebauer, J.; Blechert, S. *Synlett* **2005**, *18*, 2826.

[55] Lebouc, A.; Delaunay, J.; Riobé, O. *Synthesis* **1979**, *8*, 610; Schmidt, B. *J. Org. Chem.* **2004**, *69*, 7672.

[56] 1-cyclopentenylmagnesium bromide was generously provided by K. E. O. Ylijoki.

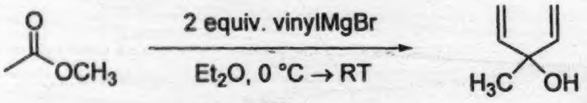
[57] The two reported methods of preparation (Berg-Nielsen, K.; Skatteboel, L. *Acta Chem. Scand. B* **1978**, *B32*, 553) were not attempted due to the ready availability of the Grignard reagent. Future work should explore these synthetic routes since the Grignard reagent contained considerable impurities.


MgBr
i
ii
H_3C
OH

61

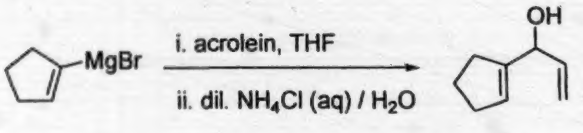
Conditions: i. crotonaldehyde, THF, 0 °C→ RT
ii. *n*BuLi, Et_2O, -78 °C → 0 °C; crotonaldehyde, Et_2O,
-78 °C → RT (49%); then $LiAlH_4$•NaOMe, THF, 65 °C, 2d (85%)

Scheme 2.10


O
OCH3
2 equiv. vinylMgBr
Et2O, 0 °C → RT
70%
H3C
OH

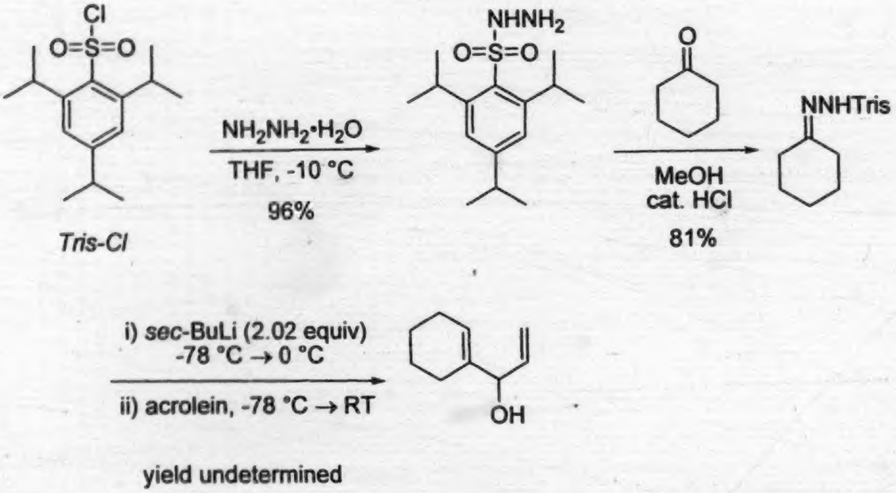
63

Eq 2.2


MgBr
i. acrolein, THF
ii. dil. NH4Cl (aq) / H2O
OH

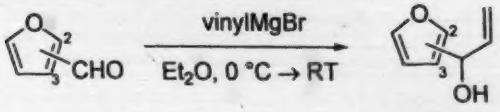
64

Eq 2.3


Cl
O=S=O
Tris-Cl
NH2NH2•H2O
THF, -10 °C
96%
NHNH2
O=S=O
O
MeOH
cat. HCl
81%
NNHTris
i) sec-BuLi (2.02 equiv)
-78 °C → 0 °C
ii) acrolein, -78 °C → RT
yield undetermined
OH

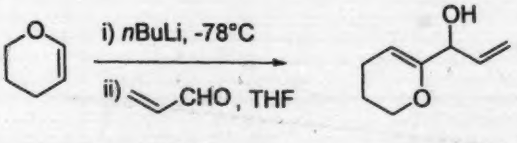
65

Scheme 2.11


vinylMgBr
Et₂O, 0 °C → RT
CHO
OH
2
3

2-furanyl, **66**, 78%
3-furanyl, **67**, 94%

Scheme 2.12

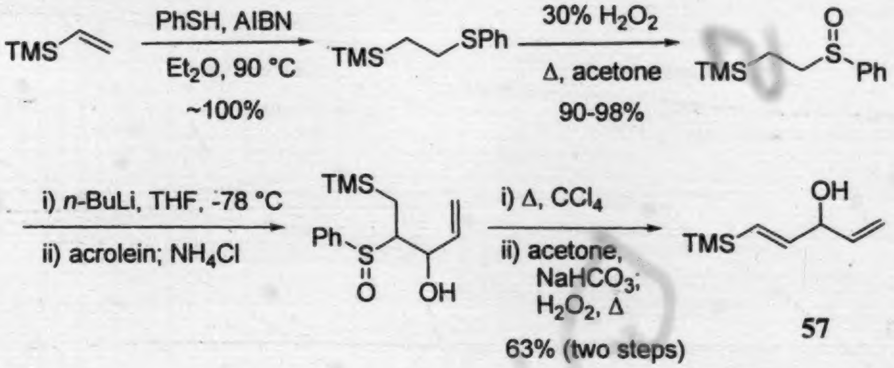

i) nBuLi, -78°C
ii) CHO, THF
OH
O

42%

68

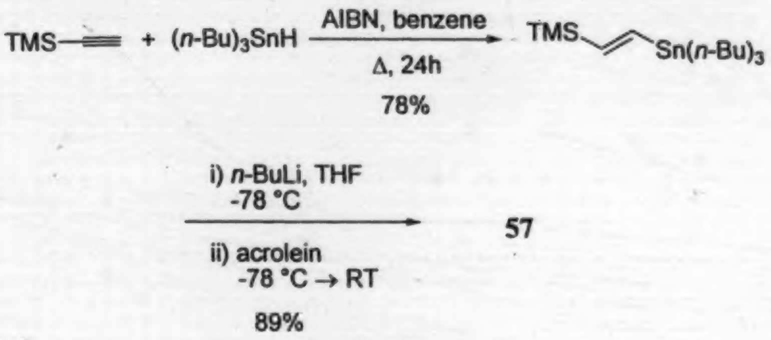
Eq 2.4

The syntheses of many of the dienol substrates were easily accomplished. Other cases, however, did not proceed with the ease, success, and/or purity reported in the literature. Most alkyl-substituted dienols were sensitive to acidic conditions; those with greater substitution were more easily dehydrated, decomposing mostly to cyclized Nazarov products. The furanyl-substituted dienols (**66**, **67**) were also sensitive to light and air. Both synthetic routes from the literature were attempted to acccess 1-Me_3Si-pentadienol (**57**), but the $SnBu_3H$ synthesis provided better yields and product purity (Schemes **2.13** and **2.14**).[43,44]


TMS
PhSH, AIBN
Et₂O, 90 °C
~100%
TMS
SPh
30% H₂O₂
Δ, acetone
90-98%
TMS
O
S
Ph
i) n-BuLi, THF, -78 °C
ii) acrolein; NH₄Cl
TMS
Ph
S
O
OH
i) Δ, CCl₄
ii) acetone, NaHCO₃, H₂O₂, Δ
63% (two steps)
OH
TMS

57

Scheme 2.13



Scheme 2.14

Following the synthesis of the substituted 1,4-pentadien-3-ols, the synthesis of substituted η^5-pentadienyl complexes was accomplished using the previously optimized conditions (Table **2.1**, conditions **G**). Dienol substrates **55** - **63** were converted to the respective pentadienyl complexes **72** - **80** in moderate to good yield (Table **2.2**). As in the case of the synthesis of Cp*Co(pentadienyl) complexes, increased alkyl substitution on the pentadienol created difficulty in the formation of the pentadienyl complex (e.g., **64**, **65**, **68** and **70**). All of the pentadienyl complexes were purified by silica gel chromatography on the bench to remove trace impurities and subsequently recrystallized by pin-hole diffusion[58] (dichloromethane and diethyl ether) to produce analytically pure material. Some complexes with bulky or multiple substitution – complexes **73**, **75**, **76**, **77**, **78**, and **80** – required several recrystallizations to achieve sufficient purity for elemental analysis or even uncontaminated NMR spectroscopy.

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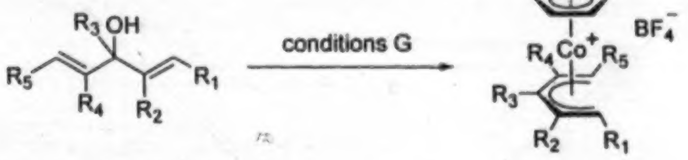
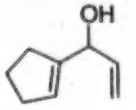
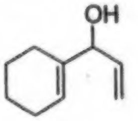
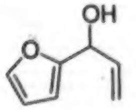
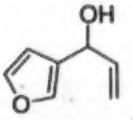
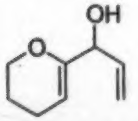
[58] See Experimental Section for further description.

Table 2.2. Synthesis of substituted cationic CpCo(η^5-pentadienyl) complexes


R3 OH
R5
R4
R2
R1
conditions G
Co+
BF4−
R4
R5
R3
R2
R1

Dienol	Substitution Pattern	Product, Yield (%)
55	R_1 = Me, R_2-R_5 = H	**72**, 87%
56	R_1 = Ph, R_2-R_5 = H	**73**, 33-50%
57	R_1 = TMS, R_2-R_5 = H	**74**, 56%
59	[illegible], R_2 = Me, R_3-R_5 = H	**76**, 55%
60	R_1, [illegible] = Me, R_2, R_3, R_5 = H	**77**, 34%
61	R_1, [illegible] = Me, R_2-R_4 = H	**78**[a]
62	R_2 = Me, R_1, R_3-R_5 = H	**79**, 51%
63	R_1-R_2, R_4-R_5 = H, R_3 = Me	**80**, 35%
64		dec.
65		dec.
66		dec.
67		dec.
68		dec.
70	R_1 = TMS, R_5 = Me, R_2-R_5 = H	dec.

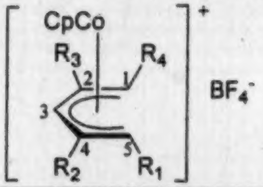
[a] Yield undetermined.

C. Pentadienyl complex characterization

The physical and spectroscopic properties of the cationic CpCo(η^5-pentadienyl) complexes **71** - **80** were similar to their Cp* analogues. The orange-red to dark-red Co(III) pentadienyl complexes were stable to air and moisture, and experienced only slight degradation (~5%) to the cobaltocenium analogue over extended periods of time.

All cyclopentadienylcobalt(η^5-pentadienyl) complexes were fully characterized, where possible, by IR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and electrospray mass spectrometry. Tables **2.3** and **2.4** summarize relevant ^{1}H and ^{13}C NMR data, respectively, for the CpCo(η^5-pentadienyl) complexes. For comparison, Table **2.5** provides the ^{1}H NMR chemical shift trends for the Cp* analogues.[3] In general, the chemical shifts on the protons of the η^5-pentadienyl ligands are approximately δ 0.70 downfield from their Cp* analogues, consistent with the greater electrophilicity of the cobalt center. As well, the ^{1}H-^{1}H coupling constants are within the expected range (based on the comparison with Cp* complexes).

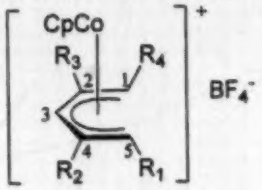
Table 2.3. Relevant ^{1}H NMR data[a] for



complex	R_1	R_2	R_3	R_4	chem shift (δ) and coupling constant (Hz)							
					H_{1endo}	H_{1exo}	H_2	H_3	H_4	H_{5endo}	H_{5exo}	Cp
71	H	H	H	H	2.08 ($^{3}J_{HH}$ = 11.7, $^{4}J_{HH}$ = 3.1)	4.28 ($^{2}J_{HH}$ = 9.5, $^{3}J_{HH}$ = 2.8)	5.90 ($^{3}J_{HH}$ = 1.0, 2.9, 6.9)	7.28 ($^{3}J_{HH}$ = 6.9, $^{4}J_{HH}$ = 1.0)	5.90 ($^{3}J_{HH}$ = 1.0, 2.9, 6.9)	2.08 ($^{3}J_{HH}$ = 11.7, $^{4}J_{HH}$ = 3.1)	4.28 ($^{2}J_{HH}$ = 9.5, $^{3}J_{HH}$ = 2.8)	5.95
72[b]	Me	H	H	H	2.07 ($^{2}J_{HH}$ = 3.2, $^{4}J_{HH}$ = 0.8)	4.21 ($^{2}J_{HH}$ = 2.8, $^{3}J_{HH}$ = 9.2, $^{4}J_{HH}$ = 0.8)	5.72-5.81	7.15 ($^{3}J_{HH}$ = 7.2, $^{4}J_{HH}$ = 0.8)	5.72-5.81	2.95	c	5.80
73	Ph	H	H	H	2.71 ($^{2}J_{HH}$ = 3.2, $^{3}J_{HH}$ = 11.9)	4.47 ($^{2}J_{HH}$ = 2.8, $^{3}J_{HH}$ = 9.1)	5.88 ($^{3}J_{HH}$ = 6.8, 9.8, 12.0)	7.38 ($^{3}J_{HH}$ = 7.3)	6.61 ($^{3}J_{HH}$ = 7.3, 12.2)	3.85 ($^{3}J_{HH}$ = 12.0)	c	5.54
74[b]	TMS	H	H	H	2.55 ($^{3}J_{HH}$ = 12.0)	4.30 ($^{3}J_{HH}$ = 7.2)	6.05 ($^{3}J_{HH}$ = 6.0, 14.8)	7.38 ($^{3}J_{HH}$ = 6.0)	5.90	1.73 ($^{3}J_{HH}$ = 14.8)	c	5.90
79[b]	H	Me	H	H	2.15 ($^{2}J_{HH}$ = 2.6, $^{3}J_{HH}$ = 12.4)	4.22-4.28	5.80 ($^{3}J_{HH}$ = 2.4, 7.2)	7.38 ($^{3}J_{HH}$ = 7.2)	c	1.67 ($^{4}J_{HH}$ = 3.2)	c	5.86
76[b]	Me	Me	H	H	2.32-2.42 ($^{3}J_{HH}$ = 12.0, $^{4}J_{HH}$ = 0.8)	4.18 (3.0, $^{3}J_{HH}$ = 9.6)	5.62 ($^{3}J_{HH}$ = 7.3, 9.9,12.2)	7.11 ($^{3}J_{HH}$ = 7.2)	5.62	2.23	c	
77[b]	Me	H	Me	H	1.68	4.16	c	7.02	5.60-5.70	3.05	c	5.70
78[b]	Me	H	H	Me	2.54	c	5.57 ($^{3}J_{HH}$ = 6.6 Hz, $^{3}J_{HH}$ = 11.2 Hz)	7.08 ($^{3}J_{HH}$ = 7.3 Hz)	5.57 ($^{3}J_{HH}$ = 6.6 Hz, $^{3}J_{HH}$ = 11.2 Hz)	2.54	c	5.47

[a] In acetone-d_6. [b] Missing J values due to either overlapping or low-intensity signals. [c] Not applicable due to a non-hydrogen substituent.

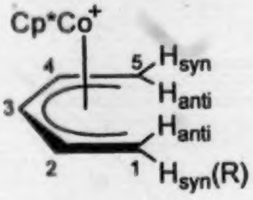
Table 2.4. Relevant ^{13}C NMR data[a] for



complex	R_1	R_2	R_3	R_4	chem shift (δ)					
					C_1	C_2	C_3	C_4	C_5	Cp
71	H	H	H	H	61.68	97.09	101.52	97.09	61.68	88.30
72	Me	H	H	H	59.99	96.58 or 95.63	97.17	96.58 or 95.63	85.42	88.52
73	Ph	H	H	H	50.20	96.20, 91.04, 85.75			b	89.33
74	TMS	H	H	H	61.70	97.52	98.91	102.30	78.39	87.46
79	H	Me	H	H	62[c]	95.24	100.80	b	61[c]	88.68
76	Me	Me	H	H	60.40	93.57	97.91	20.05	81.41	89.02

[a] In acetone-d_6. [b] Missing values due to low-intensity signals. [c] Value determined from gHMQC or gHSQC correlation.

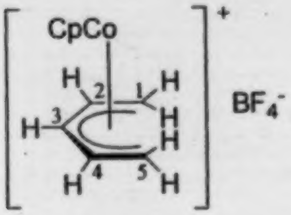
Table 2.5. ^{1}H NMR Chemical Shift Trends for Cp*Co(η^5-pentadienyl) complexes (acetone-d_6)[3]



H	δ (ppm)	*J* (Hz)
1_{anti}	1.68-2.37	*J* = 2.8-3.4, *J* = 12.1-12.4
1_{syn}	3.22-3.50	*J* = 2.8-3.4, *J* = 9.7
2	5.32-5.35	*J* = 6.9, *J* = 9.7, *J* = 12.1-12.4
3	6.34-6.52	*J* = 6.9-7.3
4	5.07-5.35	*J* = 6.9-7.3, *J* = 9.5-10.0, *J* = 11.9-12.4
5_{anti}	1.97-2.35	*J* = 2.0-2.4, *J* = 2.8-4.2, *J* = 11.9-12.4
5_{syn}	3.16-3.57	*J* = 2.8-4.2, *J* = 9.5-10.0

As a representative example, the characterization of the parent pentadienyl complex **71** is detailed here (Figure **2.1**). The molecular composition of **71** was obtained from electrospray ionization mass spectrometry and confirmed for the bulk material by elemental analysis. Infrared spectroscopy verified the presence of alkene moieties – by $\nu_{C\text{-}H}$ (3078 cm^{-1}) and $\nu_{C\text{-}C}$ (1520, 1455, 1431 cm^{-1}) stretching frequencies – as well as by the absence of the hydroxyl absorption from the starting pentadienol.

Figure 2.1. $[CpCo(\eta^5\text{-pentadienyl})]^+BF_4^-$ (71)



Proton NMR spectroscopy confirmed the structural assignments by chemical shift, multiplicity, integration and coupling constants. Even though there are twelve protons in the complex, only five signals appear in the NMR spectrum due to symmetry of both ligands (Table **2.3**). The most downfield signal (δ7.28, tq) is assigned to the central proton, with typical $^3J_{HH}$ coupling to the two neighboring protons (H_2 and H_4) and small $^4J_{HH}$ coupling to the four protons at the termini. The next signal upfield (δ 5.95, s) is assigned to the five protons of the cyclopentadienyl ancillary ligand, based on relative chemical shift (δ 5.3-6.0), integration (5H), and multiplicity. The protons H_2 and H_4 are assigned to the signal appearing at δ 5.90. This doublet of doublet of doublet integrates to two protons and exhibits $^3J_{HH}$ coupling to H_3 (6.8 Hz), H_{1exo} (9.4 Hz, *cis*) and H_{1endo} (16.4 Hz, *trans*). The doublet of doublet at δ 4.28 is assigned to the two terminal *exo* protons. The *exo* protons are less shielded than the terminal *endo* protons (δ2.03). The *exo* protons couple to H_{1endo}/H_{5endo} ($^2J_{HH}$, 2.8 Hz) and H_2/H_4 ($^3J_{HH}$, 9.5 Hz), and the *endo* protons couple to H_{1exo}/H_{5exo} ($^2J_{HH}$, 3.1 Hz), and H_3 ($^4J_{HH}$, 0.8 Hz). The *trans* coupling for the *endo* protons is uncertain due to the difficulty of assigning the precise coupling constant in the presence of overlap with the solvent peak.

Correlations between the protons assigned above were confirmed by 2D ^{1}H NMR spectroscopy (GCOSY). The central proton (H_3) is coupled to all the other protons. Protons at positions 2 and 4 are coupled to the terminal protons, and the terminal protons are coupled to each other. Taken together, the ^{1}H NMR data unambiguously support the structure of a CpCo(η^5-pentadienyl) complex.

The four signals in the ^{13}C NMR spectrum confirm the symmetry observed in the ^{1}H NMR spectrum. The signals (δ 62-102) fall upfield of the expected range (δ 110-140) for alkene protons due to shielding from the coordinated cobalt. The central carbon is expected to be the most downfield due to higher carbon branching. The Cp carbons are similar to the C_2/C_4 carbons, but are expected to be further upfield due to decreased bond angle of the carbocycle in comparison with the open ligand and the consequently increased *p*-character. The terminal pentadienyl carbons are the most upfield signals, as expected from alkene ^{13}C NMR trends.

The carbon assignments were confirmed by the correlated gHMQC and gHMBC NMR spectra. In the gHMQC spectrum, each of the carbons was correlated with the expected protons based on the ^{1}H and ^{13}C NMR assignments suggested above. The gHMBC spectrum shows $^2J_{CH}$ coupling (C_2/C_4 with the terminal protons) and $^3J_{CH}$ coupling (the central carbon with the terminal protons, the terminal carbon with the central proton).

X-ray crystallography provided the definitive evidence that the proposed structure is indeed correct and that $[CpCo(\eta^5\text{-pentadienyl})]^+BF_4^-$ had been successfully synthesized.

The other pentadienyl complexes **72** - **80** synthesized display very similar spectroscopic data – IR stretching frequencies, chemical shifts, multiplicities, coupling constants, correlations, and elemental analysis consistent with the molecular formulae proposed. The following discussion is reserved for data that do not fit the trends established above.

For the 1-methyl substituted complex **72**, the chemical shift of δ 2.07 (H_{1endo}) in the ^1H NMR spectrum is missing the *trans* coupling constant/multiplicity due to overlap with solvent peak. One would expect to see a 12 Hz coupling to H_2, consistent with the observed correlation between H_{1endo} and H_2 in the GCOSY spectrum. Even though the gHMQC spectrum is missing the $^1H/^{13}C$ correlations for both C_2 and C_4 of **72**, one would expect the C_4 signal to be more upfield, due to higher carbon branching; the H_5/C_5 correlation, also missing from the gHMQC spectrum, is easily identified by chemical shift in the one-dimensional ^{13}C NMR spectrum.

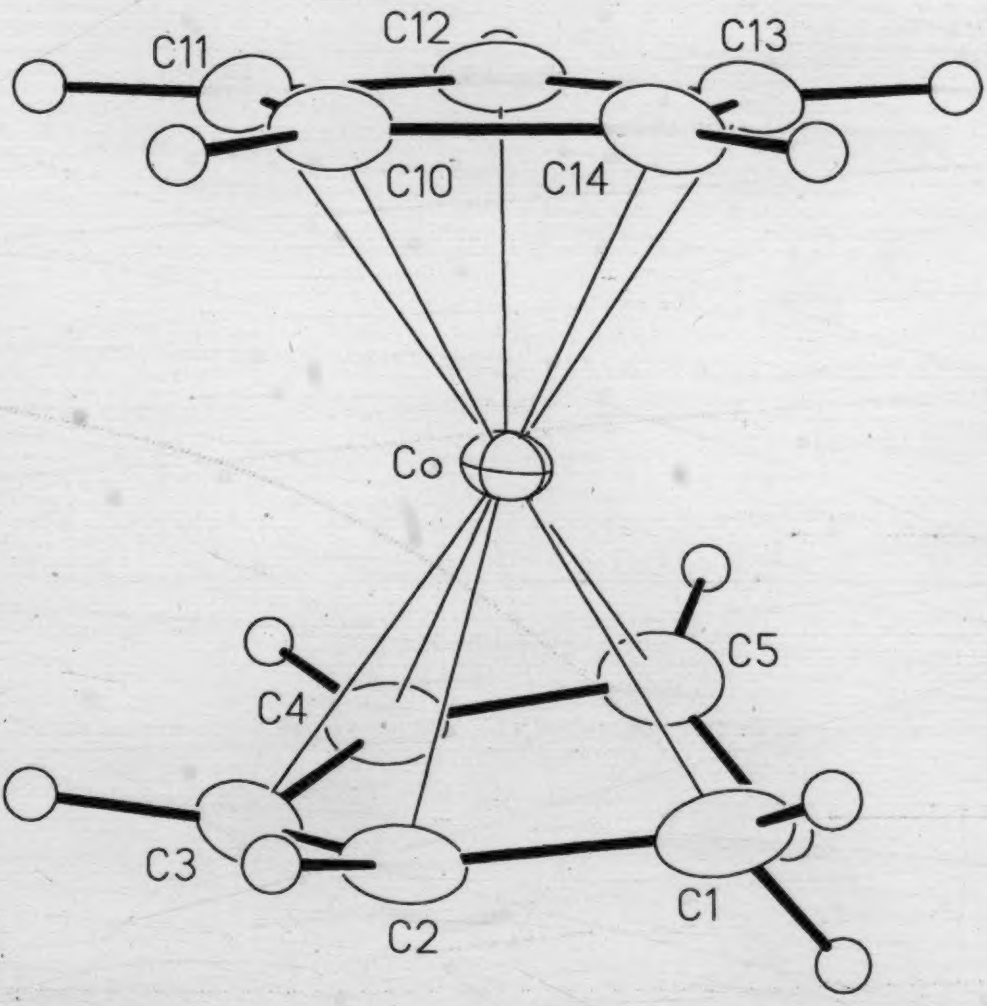
Neither column chromatography nor recrystallization by pin-hole diffusion (dichloromethane and ether) resulted in an analytically pure sample of 1-phenylpentadienyl complex **73**. The chemical shifts of **73** were generally ~0.1 - 0.2 ppm further downfield from other CpCo(pentadienyl) complexes, presumably due to the deshielding effect of the phenyl substituent. As well, the proton geminal to the phenyl substituent was downfield by 0.40 ppm and the vicinal proton 0.9 ppm further downfield than the 1-methylpentadienyl complex **72**. The geminal proton (H_5) of 1-trimethylsilylpentadienyl complex **74**, on the other hand, appears ~0.4 ppm upfield from that in **72** due to the shielding effect of the TMS substituent. Carbon-5 in **74** resonates further downfield than C_5 of **72**, due to the heavy atom effect.

The 1,2-dimethylpentadienyl complex **76** was purified by column chromatography for spectroscopic analysis, yet even after repeated recrystallizations, an analytically pure sample could not be obtained. The 1,4-dimethylpentadienyl complex **77** appears to exist as a mixture with cobaltocenium, suggested by the presence of two Cp signals in the ^{1}H NMR spectrum. The ^{13}C NMR chemical shift for the C_7 methyl substituent of complex **76** was determined by correlations in the gHSQC spectrum, since it was missing from the APT ^{13}C NMR spectrum. The 2-methylpentadienyl complex **79** is missing the ^{13}C NMR signal for the quaternary C_4, a common phenomenon for quaternary carbon signals in ^{13}C NMR spectroscopy.

X-ray quality crystals were obtained by recrystallization by using pin-hole diffusion for four of the η^5-pentadienyl complexes (**71**, **72**, **74**, **79**; Figures **2.2** – **2.5**). Figure **2.6** and Tables **2.6** – **2.8** below summarize the significant bond lengths (C-C and Co-C) and bond angles for the variously substituted pentadienyl complexes that have been structurally characterized by X-ray crystallography.

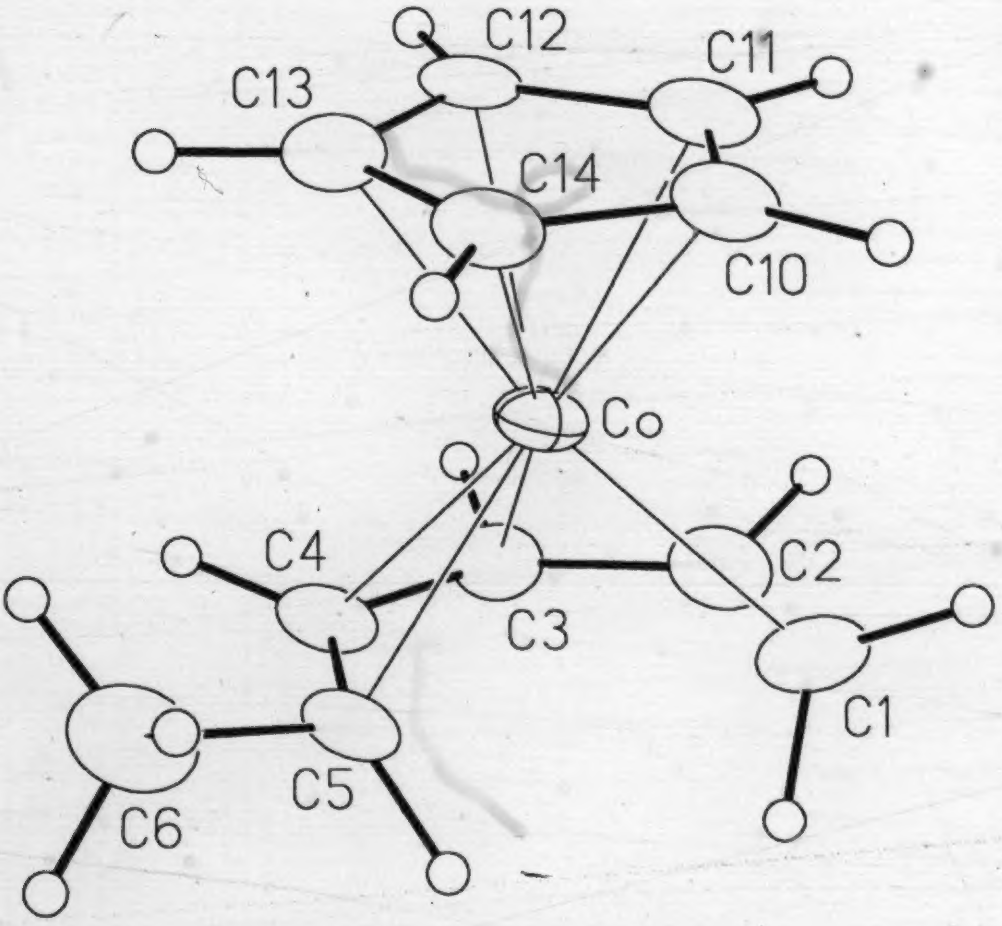
From a comparison of the various C-C bond lengths in the pentadienyl ligands, it appears that the bonds are not equivalent in character, even in the case of the unsubstituted ligand. The 1-methyl- and 1-trimethylsilylpentadienyl ligands in **72** and **74**, respectively, appear closer to an η^3,η^2-coordination mode, based on the variability in the C-C bond lengths. The 2-methylpentadienyl ligand in **79**, however, reflects a different pattern, possibly reflecting an η^2,η^2,η^1-coordination mode. These trends in the coordination modes of the pentadienyl ligands will be discussed in Chapter Four in relation to the reactivity of each complex in alkyne cycloaddition reactions.

Figure 2.2. ORTEP for Complex **71** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0603


C11
C12
C13
C10
C14
Co
C5
C4
C3
C1
C2

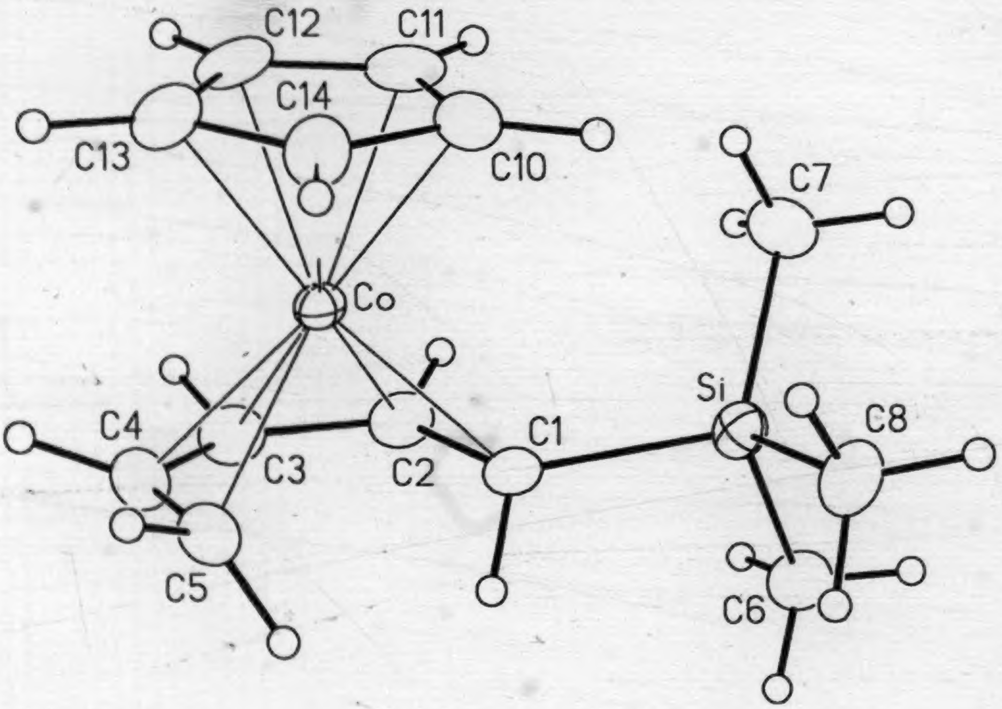
Final Residuals: $R_1 = 0.0547$; $wR_2 = 0.1520$. Data obtained at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Figure 2.3. ORTEP for Complex **72** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0581


C12
C11
C13
C14
C10
Co
C4
C2
C3
C1
C5
C6

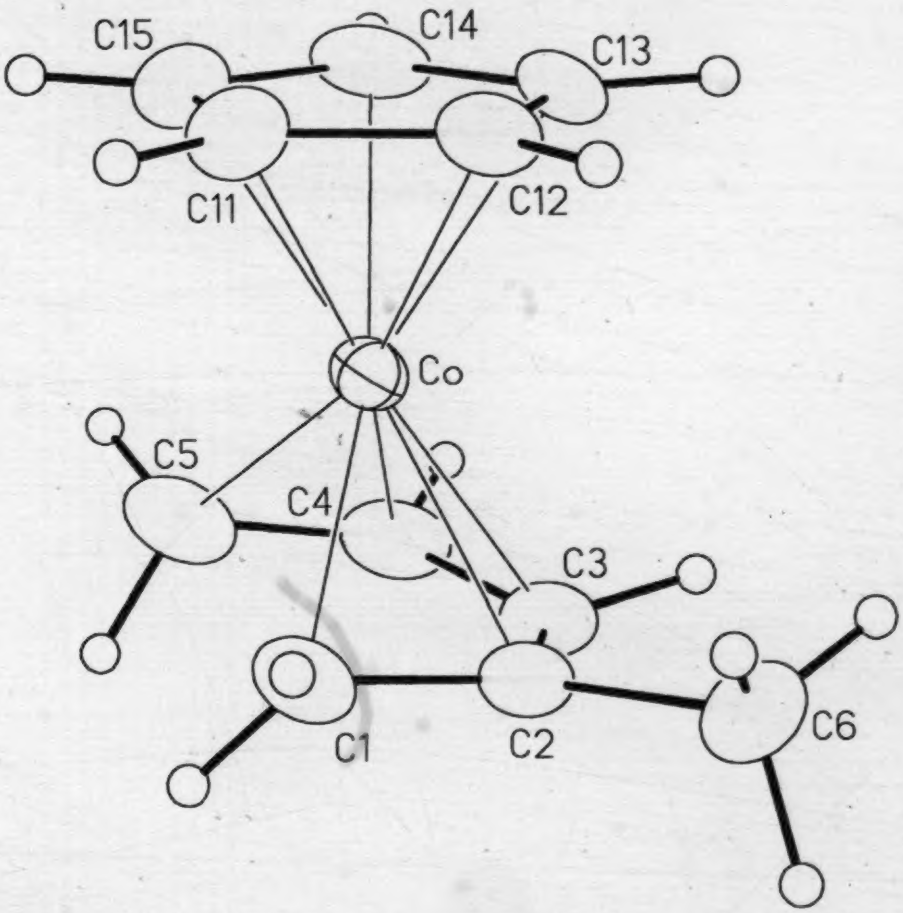
Final Residuals: $R_1 = 0.0645$; $wR_2 = 0.1720$. Data obtained at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Figure 2.4. ORTEP for Complex **74** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0704


C12
C11
C14
C13
C10
C7
Co
Si
C8
C4
C1
C3
C2
C5
C6

Final Residuals: $R_1 = 0.0464$; $wR_2 = 0.1400$. Data obtained at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Figure 2.5. ORTEP for Complex **79** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0642



C15
C14
C13
C11
C12
Co
C5
C4
C3
C1
C2
C6

Final Residuals: $R_1 = 0.0350$, $wR_2 = 0.0958$. Data obtained at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Figure 2.6. C-C bond lengths of pentadienyl ligands of CpCo-pentadienyl complexes

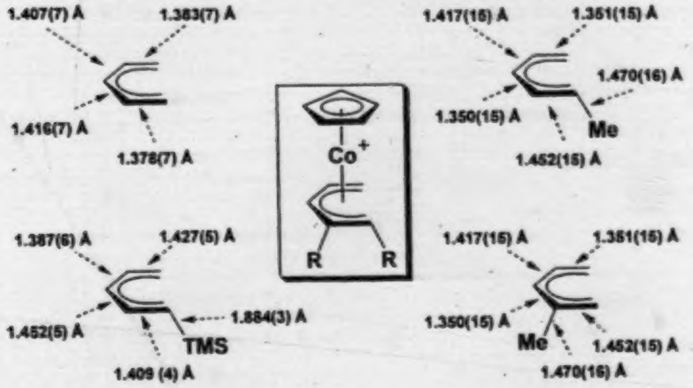

1.407(7) Å
1.383(7) Å
1.416(7) Å
1.378(7) Å
Co+
R
R
1.417(15) Å
1.351(15) Å
1.470(16) Å
1.350(15) Å
Me
1.452(15) Å
1.387(6) Å
1.427(5) Å
1.884(3) Å
1.452(5) Å
TMS
1.409 (4) Å
1.417(15) Å
1.351(15) Å
1.350(15) Å
Me
1.452(15) Å
1.470(16) Å

Table 2.6. C-C bond lengths (Å) of pentadienyl ligands of $[CpCo(\eta^5\text{-pentadienyl})]^+BF_4^-$ complexes

	parent	*1-Me*	*1-TMS*	*2-Me*
C1-C2	1.383(7)	1.452(15)	1.409(4)	1.403(7)
C2-C3	1.407(7)	1.350(15)	1.452(5)	1.412(6)
C3-C4	1.416(7)	1.417(15)	1.387(6)	1.369(7)
C4-C5	1.378(7)	1.351(15)	1.427(5)	1.409(8)
C1/2-C6	---	1.470(16)	—	1.508(6)
C1-Si	---	---	1.884(3)	—

Table 2.7. Co-C bond lengths (Å) of pentadienyl ligands of $[CpCo(\eta^5\text{-pentadienyl})]^+BF_4^-$ complexes

	parent	*1-Me*	*1-TMS*	*2-Me*
Co-C1	2.106(5)	2.095(9)	2.149(3)	2.084(6)
Co-C2	2.028(4)	2.024(10)	2.029(3)	2.060(4)
Co-C3	2.039(4)	2.011(9)	2.033(3)	2.053(4)
Co-C4	2.012(4)	2.076(10)	2.028(3)	2.021(4)
Co-C5	2.092(5)	2.131(11)	2.096(3)	2.094(4)

Table 2.8. C-C-C bond angles (deg.) of pentadienyl ligands of $[CpCo(\eta^5\text{-pentadienyl})]^+BF_4^-$ complexes

	parent	*1-Me*	*1-TMS*	*2-Me*
C1-C2-C3	123.7 (5)	122.1(12)	123.3(3)	121.5(4)
C2-C3-C4	122.3(4)	128.3(12)	124,8(3)	126.0(5)
C3-C4-C5	125.0(5)	121.9(12)	125.4(3)	125.5(5)
C6(Si)-C1-C2	—	117.7(12)	125.3(2)	120.2(4)/117.6(4)
C11-C10-C14	109.1(4)	109.1(10)	107.3(3)	108.4(4)
C10-C11-C12	107.5(4)	106.6(10)	107.3(3)	107.6(4)
C11-C12-C13	107.6(4)	109.3(9)	110.0(3)	106.2(4)
C12-C13-C14	107.5(4)	108.2(9)	106.6(4)	108.3(5)
C10-C14-C13	108.3(4)	106.9(9)	108.7(3)	109.5(5)

III. Conclusion

The synthesis of novel CpCo(η^5-pentadienyl) complexes has been achieved in good to moderate yields from cobalt bis(ethylene) complex **34**. Most of the products were successfully purified (by silica gel column chromatography and recrystallization using pin-hole diffusion) and characterized (^{1}H and ^{13}C NMR, mass spectrometry, infrared spectrometry, elemental analysis and, for selected compounds, X-ray crystallography). Certain substitutions patterns, such as furanyl- and dihydropyranyl-substituted pentadienols, proved inaccessible. Too many substituents as well as the phenyl substituent appear to destabilize the η^5-coordination mode. A modest range of pentadienyl complexes was thus assembled for further reactivity studies toward [5+2] cycloaddition reactions with alkynes.

Chapter Three: Cyclopentadienylcobalt dicarbonyl and the synthesis of (η^3-pentadienyl)carbonyl- and (η^5-pentadienyl) complexes

I. Background of $CpCo(CO)_2$ (35) and CpCo(η^3-pentadienyl)CO complexes

A. Synthesis and use of starting complex 35

Cyclopentadienylcobalt dicarbonyl (**35**) has played a central role in the development of the organometallic chemistry of cobalt. By the 1980's, many cobalt dienyl, diene and π-allyl complexes had been made – due, in large part, to the availability, ease of use and reactivity of **35**. Much of the recent interest has been in the area of cycloaddition reactions catalyzed by **35** (see representative examples in Scheme **3.1**).[59,60,61,62,63] So much work has been done, in fact, that **35** has been identified as "the most extensively developed system" for cobalt.[64,65]

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[59] Kemmitt, R. D. W.; Russell, D. R., In *Comprehensive Organometallic Chemistry*, Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, **1982**, *5*, 1. Sweany, R. L., In *Comprehensive Organometallic Chemistry II*, Abel, E. W.; Stone, F. G. A.; Wilkinson, G.; Atwood, J. D., Eds.; Pergamon: Oxford, **1995**, *8*, 1.

[60] [1,5-COD ligand exchange]: King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593. Nakamura, A.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 452. King, R. B., In *Organometallic Syntheses*, Eisch, J. J.; King, R. B., Eds.; Academic: New York, 1965, Vol. 1, p.131.

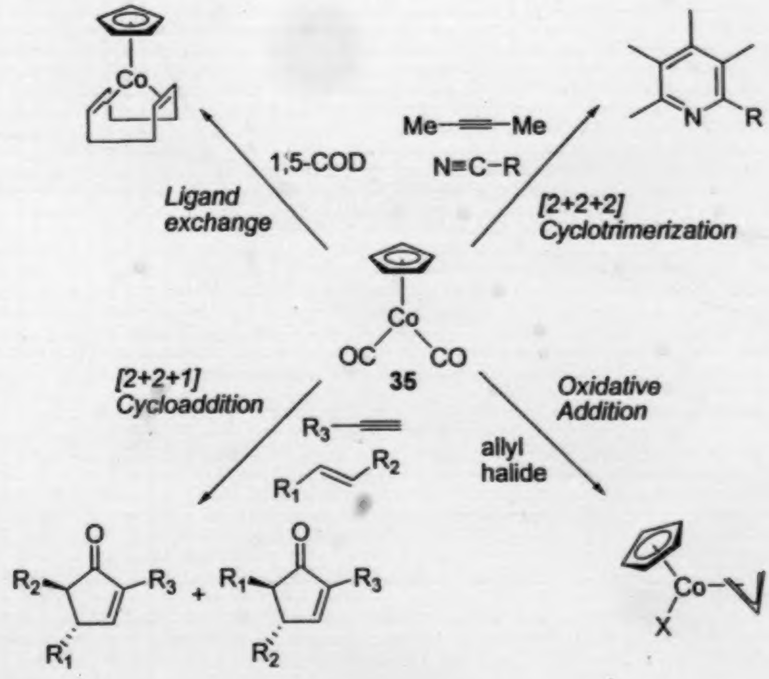
[61] {[2+2+2] Cyclotrimerization}: Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1973**, 280. Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383. Bönnemann, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248. Bönnemann, H.; Brijoux, W., In *Aspects of Homogeneous Catalysis.* Ugo, R., Ed.; Reidel: Dordrecht, 1984; Vol. 5, p.75. Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26. Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W. *Helv. Chim. Acta.* **1984**, *67*, 1616.

[62] [Pauson-Khand reaction]: Blanco-Urgoiti, J.; Añorbe, L.; Pérez-Serrano, L.; Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* **2004**, *33*, 32, and references therein.

[63] [Oxidative addition]: Aviles, T.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1116.

[64] Malacria, M., Aubert, C., Renaud, J.-L. "Organometallic Complexes of Cobalt" In *Science of Synthesis*, Thieme: New York, 2001, p.439.

[65] For examples, see Vollhardt, K. P. C., *Acc. Chem. Res.* **1977**, *10*, 1; Kemmitt, R. D. W. *J. Organomet. Chem.* **1981**, *211*, 279.

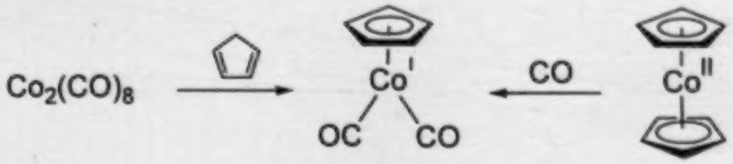

1,5-COD
Ligand exchange
Me—≡—Me
N≡C–R
[2+2+2] Cyclotrimerization
Co
OC
CO
35
[2+2+1] Cycloaddition
R3
R1
R2
Oxidative Addition
allyl halide
O
R2
R3
R1
+
Co
X
N
R

Scheme 3.1

One of advantages of complex **35**, besides its commercial availability, is its relative stability. Unlike bis(ethylene) complex **34**, the dicarbonyl complex **35** is stable in air for short periods of time. Increased air-stability opens opportunities to a wide range of synthetic chemists, both in organic and inorganic chemistry, to utilize this compound as a common starting material. Even though complex **35** is most commonly stored below room temperature (-20 °C), the compound is much less temperature-sensitive than **34** (which decomposes above -20 °C upon prolonged standing) and can be manipulated at room temperature without rapid decomposition.

The use of the dicarbonyl complex does present some challenges, however, not the least of which is its low boiling point and volatility. While commercially available, complex **35** is far from inexpensive and therefore, most chemists who use significant quantities of the compound prefer to synthesize it themselves.

There are two common routes for the synthesis of **35**, one developed by R. B. King and the other by E. O. von Fischer. In King's synthesis, cyclopentadiene undergoes an oxidative thermal displacement of carbon monoxide from dicobalt octacarbonyl to yield the product and excess cyclopentadiene becomes a hydrogen acceptor (left side of Scheme **3.2**).[64,66,67,68] Fischer's synthesis, on the other hand, is a reductive ligand exchange of one cyclopentadiene ligand with carbon monoxide in cobaltocene (**36**) (right side of Scheme **3.2**).[64,66,69] The former synthesis is preferred since it requires no special equipment, such as pressurized reaction vessels, and proceeds at significantly higher yields (93% vs. 25 %).[70] The Fischer synthesis proceeds via a disproportionation reaction to achieve the reduction, which yields at best 50% of the desired product. In the actual reaction, only half of the theoretical yield of the cobalt(I) species is formed, resulting in an overall 25% yield. More details about the King synthesis will be discussed below in the Results and Discussion section.



Scheme 3.2

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[66] King, R. B., In *Organometallic Syntheses*, Eisch, J. J.; King, R. B., Eds.; Academic: New York, 1965, Vol. 1, p. 116.
[67] Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.
[68] [Purification]: Piper, T.S.; Cotton; F. A.; Wilkinson, G. *J. Inorg. Nuclear Chem.* **1955**, *1*, 165; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1963**, 2162.
[69] Fischer, von E. O.; Jira, R. *Z. Naturforsch.* **1955**, *10b*, 354. Conditions: 90-150 °C, 200 atm CO. Note: pyridine causes decarbonylation.
[70] There is also a version of the King synthesis which activates the dicarbonyl photochemically, yet the yield is only moderate.

B. Synthesis of CpCo(η^3-allyl)CO complexes and decarbonylation reactions

1. Allyl complexation

Even with the plethora of work done with **35**, there are no examples of its use in the synthesis of CpCo(η^5-pentadienyl) complexes. There are, however, some examples of the synthesis of CpCo(allyl)L complexes (L = CO or halide). The synthesis of CpCo(*exo*-allyl)carbonyl complexes was reported by Krivykh, *et al.*[71,72] Prior to that, Aviles and Green, *et al.*, developed a synthetic route to CpCo(*endo*-crotyl)L complexes (L = halides, carbonyls, phosphines and amines).[63,73,74,75]

Historically, the synthesis of cationic CpCo(allyl)carbonyl complexes was motivated by an interest in nucleophilic addition to organometallic complexes and, in particular, the catalytic activation of small molecules such as carbon dioxide.[72,75,76] While the present endeavor does not share the same research goal, this work extends our understanding of the synthesis and reactivity of such complexes.

Krivykh, *et al.*, developed a general method to synthesize cationic allyl- and diene carbonyl complexes from Group 6 to 9 metals. This discussion, however, is focused exclusively on cobalt and, specifically, on the synthesis of CpCo(η^3-allyl)carbonyl complexes.

Cationic CpCo(allyl)(CO) complexes were obtained from the addition of an allyllic alcohol to complex **35** in the presence of an acid (Scheme 3.3). While other Group 9 metals required additional activation via UV irradiation, complex **35** reacted

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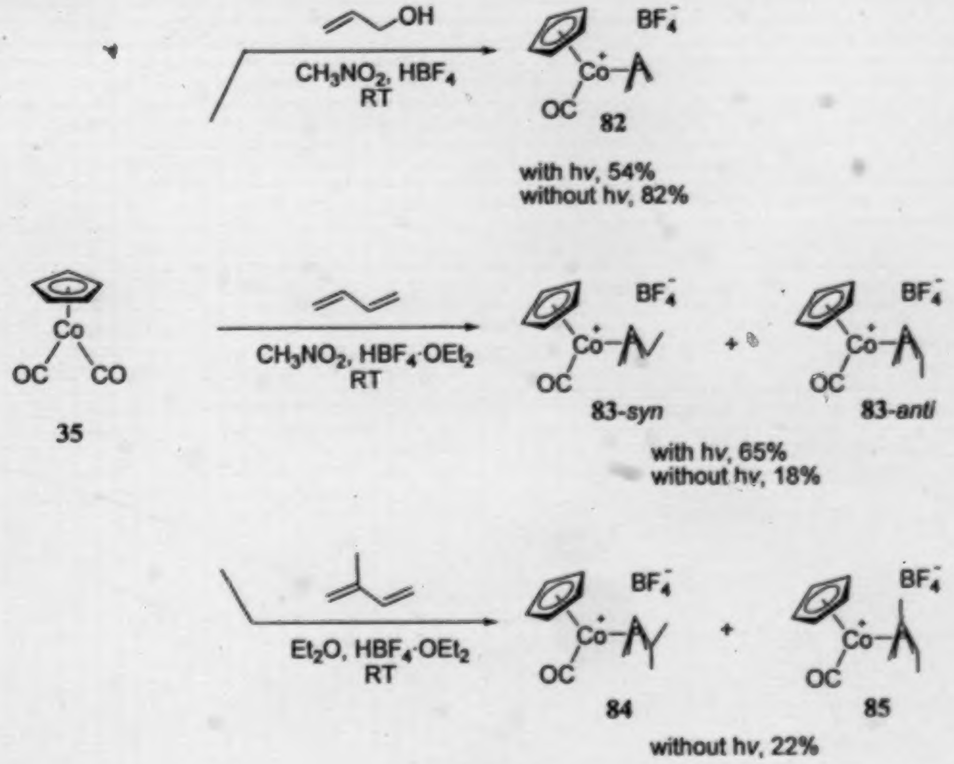
[71] Krivykh, V. V.; Gusev, O. V.; Rybinskaya, M. I. *Izv. Acad. Nauk. SSSR, Ser. Khim.* **1984**, 1178.
[72] Krivykh, V. V.; Gusev, O. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *362*, 351.
[73] Aviles, T.; Barroso, F.; Royo, P. *J. Organomet. Chem.* **1982**, *236*, 101.
[74] Aviles, T., Barroso, F., Royo, P. *J. Organomet. Chem.* **1987**, *326*, 423.
[75] Teixeira, M. G.; Paolucci, F.; Marcaccio, M.; Aviles, T.; Paradisi, C.; Maran, F.; Roffia, S. *Organometallics* **1998**, *17*, 1297.
[76] Silverman, G. S.; Strickland, S.; Nicholas, K. M. *Organometallics* **1986**, *5*, 2117.

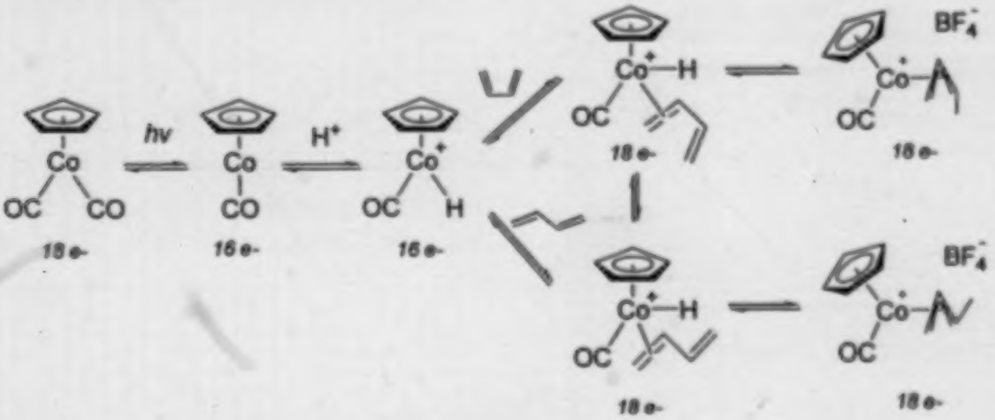
thermally over a brief period of time (0.5 h) without photo-excitation. For Rh and Ir, UV irradiation promotes the loss of one of the carbonyl ligands, providing an open coordination site for the allylic alcohol to bind. After coordination, the hydroxyl group is protonated (either directly or via initial protonation at the metal center) and then dehydrated to form the cationic allylcarbonyl complex. For Co, it is unknown whether the ligand substitution of an allyl alcohol proceeds through an associative or dissociative mechanism.


OH
CH_3NO_2, HBF_4
RT
BF_4^-
Co
OC
82
with hv, 54%
without hv, 82%
Co
OC
CO
35
CH_3NO_2, $HBF_4 \cdot OEt_2$
RT
BF_4^-
83-*syn*
+
83-*anti*
with hv, 65%
without hv, 18%
Et_2O, $HBF_4 \cdot OEt_2$
RT
84
+
85
without hv, 22%

Scheme 3.3

Three different crotyl complexes were prepared by Krivykh, *et al.* (Scheme 3.3).[72] In the case of 1,3-butadiene protonation, Krivykh observed the formation of mixtures of *syn*/*anti*-isomers of crotyl CO complex 83. In the case of 2-methyl-1,3-butadiene, a mixture of dimethyl-crotyl CO complex 84 and *anti*-crotyl-methallyl CO complex 85 was obtained.[77] While UV irradiation decreased yield in the case of the allyl alcohol, the yield and reaction time of the complexation of 1,3-butadiene was significantly improved (65%, 8h, with UV; 18%, 24h, without UV) with UV irradiation.

Krivykh suggests, based upon Tolman's work on metal-hydride addition to dienes in nickel complexes, that the formation of the *anti*-conformer supports the initial formation of a metal hydride (Scheme 3.4).[78] The diene can bind to the metal in either conformation, satisfying the 18-electron rule. The configuration of the resulting complex suggests that the diene is protonated only after binding to the metal. As well, the metal-hydride complex was proposed based on IR spectroscopy (comparing CO stretching frequencies of starting material and final product with an observed intermediate). Unfortunately, Krivykh did not report any results related to the synthesis of crotyl complexes from substituted allyl alcohols.



Scheme 3.4

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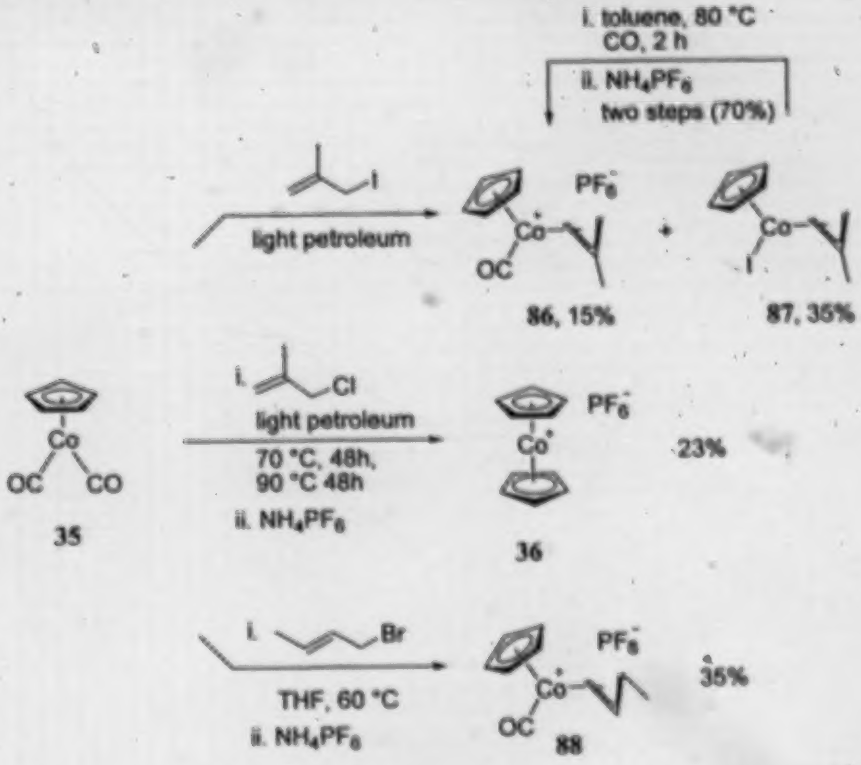
[77] A full discussion of stereochemical analysis (*endo*/*exo*, *syn*/*anti*) will be reserved for the discussion of the NMR data in the Results and Discussion section.
[78] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 6785.

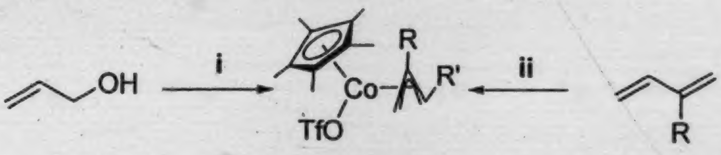
Where Krivykh's work was limited to the synthesis of CpCo(crotyl) carbonyl complexes, Aviles achieved the synthesis of simple 2-methallyl carbonyl complex **86** in good yield (Scheme 3.5). Aviles utilized 1-iodo-2-methylpropane to afford a mixture of the cationic methallyl carbonyl (15%) and the neutral methallyl iodide (35%). The iodide was then converted (with heat and bubbling carbon monoxide) to the cationic carbonyl complex (70% yield). When the reaction was attempted with 1-chloro-2-methylpropane, Aviles only observed the formation of decomposition product **36**.


i. toluene, 80 °C
CO, 2 h
ii. NH4PF6
two steps (70%)
light petroleum
PF6⁻
Co
OC
I
86, 15%
87, 35%
i.
Cl
light petroleum
70 °C, 48h,
90 °C 48h
ii. NH4PF6
Co
OC
CO
35
36
23%
i.
Br
THF, 60 °C
ii. NH4PF6
88
35%

Scheme 3.5

Aviles also synthesized a crotylcarbonyl complex (Scheme 3.5). Two significant differences between the Aviles and Krivykh crotyl synthesis are the yield and nature of the product. Aviles obtained a much lower yield (35%) than Krivykh (65%), and the reaction exclusively formed the *endo*-isomer, which was inaccessible using Krivykh's methods. No explanation is given as to configuration or mechanism of complexation; however, oxidative addition (Aviles) seems to favor *endo* formation while ligand substitution/hydride migration (Krivykh), *exo*.

Recently, the Stryker group has reported the synthesis of Cp*Co(L^1)L^2 complexes (L^1 = halide, OTf; L^2 = allyl, crotyl, methallyl) (Scheme 3.6).[10] Unlike the case of Cp, ligand exchange with Cp*Co$(CO)_2$ was poor-yielding and required harsh conditions; whereas, ligand exchange with Cp*Co$(ethylene)_2$ (**47**) is both precedented and more convenient than the dicarbonyl complex. Butadiene, isoprene and other substituted dienes were exchanged with the ethylene ligands, forming the appropriate diene complexes. The triflate complexes (**89** - **91**) was accessed by addition of triflic acid at low temperature. Cp*Co(methallyl)halide and Cp*Co(crotyl)halide complexes were also accessed from **47** and the appropriate allyl halide at 45-55 °C in THF by Dzwiniel.[2]



R, R' = H, **89**
R = H, R' = Me, **90**
R, R' = Me, **91**

R = H, Me

Conditions: i. Cp*Co$(C_2H_4)_2$, TfOH, Et_2O, -78 °C → RT, 4h, ii. Cp*Co$(C_2H_4)_2$, hexanes, 65 °C, 4-12h; then step i.

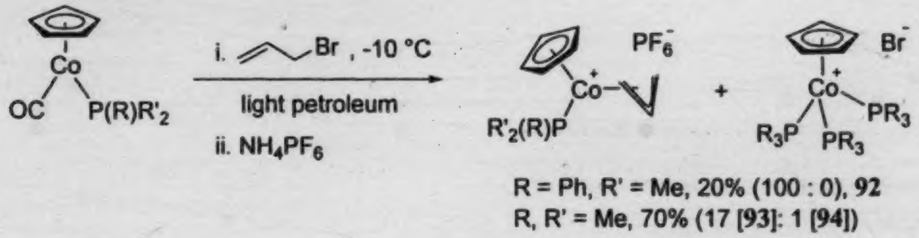
Scheme 3.6

2. Decarbonylation

While the synthesis of cationic CpCo(allyl)CO complexes is interesting, the overall goal of the project is the synthesis of cationic CpCo(η^5-pentadienyl) complexes. If we are to convert the η^3-pentadienyl to η^5-, both CO loss and geometric isomerization will be required.

Cationic η^3-allyl-carbonyl complexes have been studied primarily for their reactivity toward nucleophilic addition and not ligand substitution. The loss of the carbonyl ligand was usually considered to be disastrous, since, in the simple allyl and crotyl ligand complexes, this dissociation leads only to decomposition.[79]

There are a few examples from Aviles' work of the exchange of the carbonyl for another ligand.[63,73] In her earliest work (in the Green group) on CpCo(crotyl)L complexes (L = CO or halide), she demonstrated that a CpCo(PR_3)CO complex could be converted to CpCo(allyl)(PR_3) using allyl bromide (Scheme **3.8**). When the reaction was repeated with the trimethylphosphine starting complex, the allyl phosphine complex was formed in addition to the trisphospine bromide complex.



Scheme 3.8

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[79] In the presence of strongly polar organic solvents, such as acetonitrile and acetone, the compound is reported to have decomposed. (Fischer, von E. O.; Fischer, R. D. *Z. Naturforschg.* **1961,** *16b*, 475.)

As previously mentioned (Scheme 3.6), Aviles also discovered that when allyl iodide was added to starting complex 35, the reaction did not primarily form the CpCo(allyl)I complex, due to an equilibrium of the desired neutral product and the $[CpCo(allyl)carbonyl]^+$. The carbonyl complex could be decarbonylated by adding excess NaI , but the yield was quite low. More successful was the conversion of the iodide complex to the carbonyl complex.

During the course of the allyl iodide reaction, it was noted that a trace amount of water induced decarbonylation and formation of the black cationic aquo complex, $[CpCo(allyl)(H_2O)]^+$.[80] The aquo complex provided convenient access to other cationic CpCo(allyl)L complexes (L = phosphines, acetonitrile, $AsPh_3$, $SbPh_3$) which were difficult to access from the carbonyl complex. The acetonitrile complex in particular has been the subject of detailed electrochemical analyses.[81]

The decarbonylation of metal carbonyl complexes is a well-studied area in organometallic chemistry.[82,83,84,85] Ideal reaction conditions for decarbonylation reactions are mild, short, stepwise (involving discrete CO substitution) and high yielding. Even though classical methods, such as thermal and photochemical decarbonylation, are available, they often do not met these criteria. Therefore, methods and reagents have been developed or exploited to induce such transformations under more ideal reaction conditions. Catalytic CO exchange is a well-known process (earliest example in 1959),[86] with decarbonylation promoted by photo-induction,[87] electrocatalysis,[88] phase-transfer catalysis[89] or by means of an organic reagent[90] or transition metal.[91]

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[80] Avilés, T.; Barroso, F.; Royo, P. *J. Organomet. Chem.* **1982**, *236*, 101.
[81] Teixeira, M. G.; Paolucci, F.; Marcaccio, M.; Aviles, T.; Paradisi, C.; Maran, F.; Roffia, S. *Organometallics* **1998**, *17*, 1297.
[82] Albers, M. O., Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.
[83] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; Sausalito, CA : University Science Books, 1987, pp. 235-278.
[84] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals;* 4th Ed., Hoboken, NJ: John Wiley and Sons, 2005, pp. 87-124.
[85] Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry;* Saddle River, NJ: Prentice Hall, 1997, pp. 61-83, 138-190.

One of the most common decarbonylating reagents is trimethylamine *N*-oxide (Me_3NO). The earliest reported decarbonylation with an amine oxide (pyridine *N*-oxide) was by Hieber and Lipp in a reaction with iron pentacarbonyl to form pyridine and iron oxides.[92] Alper and Edward developed the reaction into a general method with various amine oxides and $Fe(CO)_5$.[93]

Me_3NO is inexpensive (commercially available in the anhydrous or dihydrate form), reactive at mild temperatures, and effective for removing carbonyls with IR stretching frequencies greater than 2000 cm^{-1}. Trimethylamine oxide is also effective in donor solvents such as acetonitrile, often allowing for the isolation of the decarbonylated acetonitrile complex. In most instances, the acetonitrile ligand on these complexes can then be easily replaced under mild reaction conditions.[94]

C. Synthetic rationale for CpCo(η^5-pentadienyl) complexes from 35

One can easily imagine two hypothetical routes to access η^5-pentadienyl complexes (e.g., **39**) from **35**, based upon literature precedent for making η^3-allyl cobalt complexes (Scheme 3.9). The ideal synthetic route, in our opinion, starts with pentadienol precursors **37** or **38**. The alcohol is readily accessible, while the halide must be synthesized from the alcohol, requiring an additional step. In addition, the oxidative addition of substituted allyl halides **40** and **41** to cobalt(I) dicarbonyl is relatively less successful, as shown by Aviles. Importantly, the dienols converge with the traditional methodology of organic synthesis, which incorporates such substrates into strategies involving the Nazarov cyclization.[95,96] The synthesis of the requisite non-conjugated dienols has been described in Chapter Two.

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[86] Webb, A. N.; Mitchell, J. J. *J. Phys. Chem.* **1959**, *63*, 1878.

[87] Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *330*, 80; Wegman, R. W.; Brown, T. L. *Organometallics* **1982**, *1*, 47.

[88] Julian, M.; Chanon, M. *Chem. Ber.* **1982**, 558; Chanon, M.; Tobe, M.L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1.

[89] Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183.

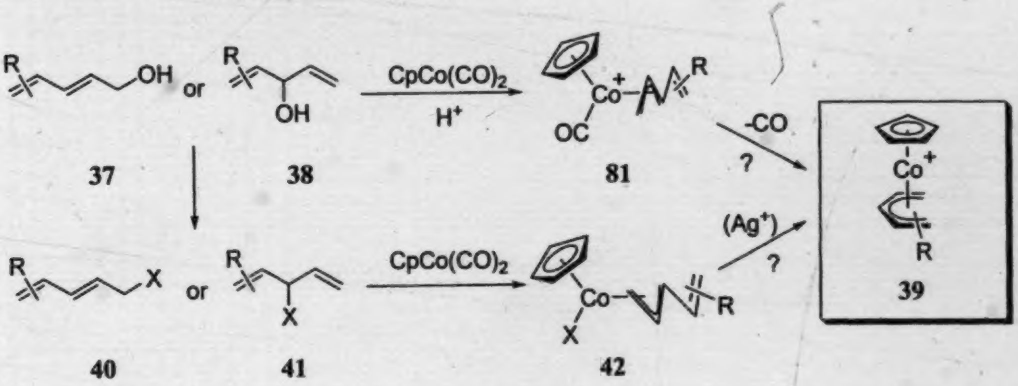
[90] Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Riegerand, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442.

[91] Albers, M. O.; Coville, N. J.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1982**, 1069.

[92] Hieber, W.; Lipp, A. *Chem. Ber.* **1959**, *92*, 2085.

[93] Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*, 1543.

[94] Albers, M. O., Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227-259.



Scheme 3.9

Pentadienol substrates, based on an extension of Krivykh's work, could in principle be used directly and added to cobalt under acidic conditions. Based on the behaviour of crotyl and allyl complexes of cobalt, there is a distinct possibility that only one of the two carbonyl ligands will be labile. If so, decarbonylation will be required to transform the η^3-pentadienyl intermediate **81** or **42** to the desired η^5-pentadienyl

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[95] Denmark, S.; Habermas, K. L.; Jones, T. K. *Org. React.* **1994**, *45*, 1.
[96] Denmark, S. "The Nazarov and Related Cationic Cyclizations" In *Comprehensive Organic Synthesis,* Vol. 5, Paquette, L. A., Ed.; Pergamon Press: Oxford, 1991, pp. 751-784.

complex. If, however, both carbonyl ligands are labile, the pentadienol could provide a direct single-step route for the synthesis of cobalt η^5-pentadienyl complexes.

D. Project Goal

The goal of the second part of this project was to determine the viability of synthesizing cyclopentadienyl cobalt (η^5-pentadienyl) complexes from dicarbonyl complex **35** and non-conjugated pentadienols. The intermediate CpCo(η^3-pentadienyl)CO complex, if isolated, would be converted to the η^5-pentadienyl complex upon induced decarbonylation.

II. Results and Discussion

A. η^3-Pentadienyl carbonyl complexes

In order to test the complexation of the pentadienol, the cobalt dicarbonyl complex **35** was synthesized using the King synthesis, as discussed above. The crude product contained up to 35% of an impurity, identified by ^{1}H NMR spectroscopy as dicyclopentadiene.[97] After various reported purification methods were attempted,[98,99] a recrystallization method was developed based on the freezing point of **35**. The crude material was dissolved in pentane and then the solution slowly cooled to -78 °C. The desired compound crystallized and the mother liquor was removed at low temperature via cannula. Crystallization was repeated as many times as necessary to achieve high levels of purity.

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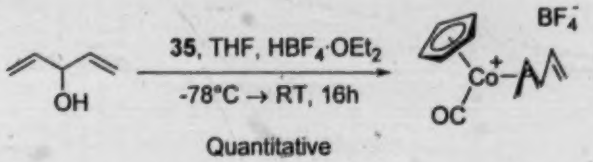
[97] The impurity was a concern due to its potential ability to inhibit coordination of the allyl substrate, even if only temporarily.

[98] [Alumina chromatography]: McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1963**, 2162. Light petroleum (b.p. 40-60 °C) was reported as the eluent.

[99] [Distillation]: Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165; King, R. B. *Inorganic Syntheses* **1963**, 7, 99 (37-38.5 °C / 2 mm Hg).

The CpCo(η^3-pentadienyl)CO complex **95** was synthesized by the thermal protonation reaction of **35** with the unsubstituted pentadienol (Eq. 3.3). The reaction was achieved on a small scale in THF in the presence of HBF$_4$·Et$_2$O at low temperature over 16 hours. These reaction conditions are similar to those of Krivykh (Scheme 3.3); THF, however, is more basic than either nitromethane or benzene. Although usually manipulated in the dry box, the compounds were, in fact, robust enough to remain under air for 12-16 hours with only slight decomposition (indicated by broadening in the ^{1}H NMR spectrum). Compound **95** was characterized by ^{1}H NMR and IR spectroscopy, and MS after purification by trituration with diethyl ether. Analysis of the reaction mixture indicated near quantitative conversion. By ^{1}H NMR spectroscopy, a small percentage (~5%) of the *anti*-isomer was also present and, upon standing at RT for two days, 5-10% of the η^5-pentadienyl complex appears; this will be discussed in further detail later. Two derivatives (**98**, **99**, *vide infra*) were recrystallized from nitromethane/diethyl ether for further purification and the preparation of X-ray quality crystals.

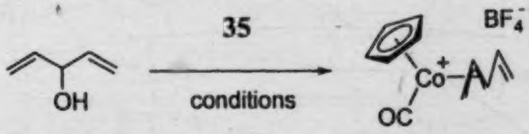


Eq. 3.3

54 **95**

The reaction, however, was not strictly reproducible, especially when attempted on larger scale. At times, the reaction produced a viscous solution that resists crystallization upon the addition of diethyl ether. One of the concerns was the competitive polymerization of the solvent; therefore, more favourable reaction conditions were explored (Table **3.1**). The unsubstituted system was used for this optimization due to the ready availability of very pure starting material, the relative success of the complexation on a small scale, and the minimization of possible steric hindrance of the substituents with the cobalt system.

Table 3.1. Synthesis of **95** – optimization studies



54 **95**

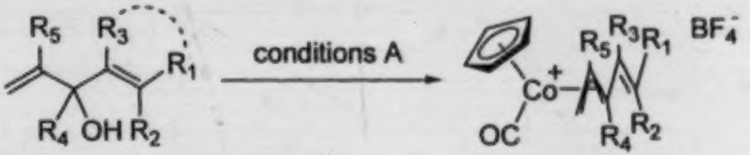
	Solvent[a]	Temperature	Time	Acid[b]	Yield
A	THF	-78 °C → RT	16 h	$HBF_4 \cdot Et_2O$	Quantitative
B	THF	RT	2 h	$HBF_4 \cdot Et_2O$	70 %
C	benzene	RT	16 h	$HBF_4 \cdot Et_2O$	dec.
D	benzene	-10 °C	16 h	$HBF_4 \cdot Et_2O$	dec.
E	CH_3NO_2	RT	0.5 h	$HBF_4 \cdot Et_2O$	dec. (<10% pdt)
F	CH_3NO_2	-30 °C	16 h	$HBF_4 \cdot Et_2O$	dec. (<10% pdt)
G	Et_2O	-78 °C	16 h	$HBF_4 \cdot Et_2O$	dec. (<10% pdt)
H	toluene	-78 °C	16 h	$HBF_4 \cdot Et_2O$	dec.
I	acetone	-78 °C	16 h	$HBF_4 \cdot Et_2O$	dec. (<10% pdt)
J	benzene	RT	16 h	$BF_3 \cdot Et_2O$	dec.
K	CH_3NO_2	RT	16 h	$BF_3 \cdot Et_2O$	dec.
L	CH_3NO_2	RT	16 h	AcOH (xs)	N.R.
M[c]	CH_3NO_2	RT	16 h	$HBF_4 \cdot Et_2O$	dec.
N	THF	-78 °C → RT	2 h	$HBF_4 \cdot Et_2O$	75%

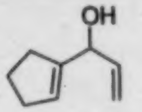
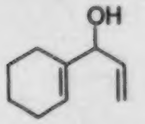
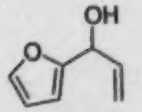
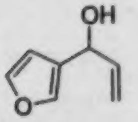
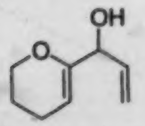
[a] Unless otherwise noted, complex concentration was 0.10-0.25M. [b] 1.1 equiv. of acid was used unless otherwise stated. [c] Complex concentration was 0.50 M.

Benzene (Entries C, D) and nitromethane (Entries E, F) were tested as solvents, since they proved successful for Krivykh in the thermal protic complexation of allyl alcohols. Neither of these, however, improved the yield. In fact, reactions in either solvent yielded mostly an unidentified compound with similar physical properties to the desired product, yet different ^{1}H NMR spectroscopy and MS results. Next, two other acids ($BF_3{\cdot}OEt_2$ and excess acetic acid) were surveyed (Entries J, K, L), with the former yielding similar decomposition products. In the case of acetic acid, no reaction occurred and only starting material was recovered. Third, the temperature conditions were adjusted (Entries B, C, E, J, K, L, M), since Krivykh achieved an 82% yield in the protic complexation of the allyl alcohol at room temperature in only half an hour. In THF, after two hours, the reaction yielded 70% at room temperature. Other attempts (in benzene and nitromethane) resulted in decomposition. All attempts, therefore, to improve the reaction conditions were unsuccessful, and the best conditions remain as first described and restricted to rather small scale (500 mg maximum).

With the conditions optimized, at least for small scale synthesis, the formation of a variety of substituted (η^3-pentadienyl)carbonyl complexes was attempted (Table **3.2**). The 1-substituted dienols (**55 - 60**) proceeded in low to good yields. The 2- and 3-substituted dienol substrates (**62 - 69**), however, produced only unidentifiable products. The unknown products formed from 2- and 3-substituted dienols had similar physical characteristics to the expected products, yet possessed different ^{1}H NMR spectra and MS results, as well as different colours (much lighter than the expected orange to dark red).

Table 3.2. Synthesis of substituted CpCo(*syn*-η^3-pentadienyl)carbonyl complexes


R5
R3
R1
R4
OH
R2
conditions A
Co+
OC
R5
R3
R1
R4
R2
BF4-

Dienol	Substitution	Product, Yield (%)
55	R^1 = Me, R^2-R^5= H	**97**, 83-90%
56	R^1 = Ph, R^2-R^5= H	**98**, 38%
57	R^1 = TMS, R^2-R^5 = H	**99**, 70%
58	R^1, R^2 = Me, R^3-R^5 = H	**100**, 42%
60	R^1, R^5 = Me, R^2-R^4 = H	**101**, 11%
62	R^2 = Me, R^1, R^3-R^5 = H	*a*
63	R^1 –R^2, R^5 = H, R^3 = Me	*a*
64		*a*
65		*a*
66		*a*
67		*a*
68		*a*

[a] Identity of product unknown.

All of the structurally identified products were characterized by ^{1}H NMR spectroscopy and electrospray MS. Although most of the 1-substituted compounds were confirmed by mass spectrometry, the unidentified products (as well as unsubstituted η^3-pentadienyl complex **95**) failed to provide any tractable mass spectrometry data. As well, satisfactory elemental analyses could not be obtained for any of the η^3-pentadienyl complexes due to the small quantities of the η^5-complex present.

While optimizing the reaction temperature, we obtained an interesting stereochemical result that had previously not been observed. Under conditions B (Table 3.1), the product was ~100% *syn* isomer and, under optimized conditions A (Table 3.1), there was only 2% of the *anti* isomer was observed. However, when the reaction mixture was warmed quickly to room temperature by removing the acetone-dry ice bath after 15 minutes and the reaction allowed to proceed for only 2 h (conditions N), the ratio of *syn* : *anti* was 71: 29. The observation and ratio of both *syn* and *anti* products under these conditions is consistent with those observed in the cationic CpCo(crotyl)carbonyl complexes reported by Krivykh, *et al.*[100]

An NMR sample of this (71 : 29) product mixture was left standing in acetone-d_6 for two days at room temperature. Isomerization exclusively to the *syn*-isomer was expected; however, little change in the ratio of *syn : anti* was observed (68 : 32). A new set of peaks (~8% overall) emerged corresponding to the known η^5-pentadienyl complex **71**. It is unknown exactly what is promoting the decarbonylation and isomerization to the η^5-pentadienyl complex, yet it appears to leave the *syn : anti* ratio unaffected.

Before discussing the decarbonylation – the background, reaction conditions, optimization, and characterization data – trends in the IR and NMR data for the η^3-pentadienyl complexes will be discussed, with an emphasis on spectroscopic anomalies and unique characteristics.

B. η^3-Pentadienyl carbonyl complexes: characterization

IR spectroscopy determined the presence and relative strength of the remaining carbonyl metal bond. The stretching frequency is within the range consistent with the reactivity of the carbonyl ligand towards assisted decarbonylation (>2000 cm^{-1}). There is little difference, however, among the carbonyl stretching frequencies of the various substituted CpCo(η^3-pentadienyl)carbonyl complexes – complexes **97** ($\nu_{C=O}$, 2075 cm^{-1}), **95** ($\nu_{C=O}$, 2078 cm^{-1}), **98** ($\nu_{C=O}$, 2080 cm^{-1}) and **99** ($\nu_{C=O}$, 2081 cm^{-1}). As a comparison, the carbonyl stretching frequencies for starting cobalt(I) dicarbonyl complex **35** are 2028 and 1967 cm^{-1}.

The discussion of the ^{1}H NMR spectroscopy encompasses two major issues related to the stereochemistry of allylmetal complexes: first, the stereochemistry of the allyl in relation to the metal (*endo* or *exo*) and second, the orientation of the R group on the terminus of the allyl in relation to the rest of the allyl (*anti* or *syn*) (Figure 3.1). Substantial literature precedes this research on the stereochemistry of (cyclopentadienyl)cobalt allyl-carbonyl complexes.[100] Krivykh's work established the kinetic preferences of the simple allyl ligands and their preferred configurations, providing NMR data and general trends for such complexes against which our CpCo(η^3-pentadienyl)carbonyl complexes can be compared.

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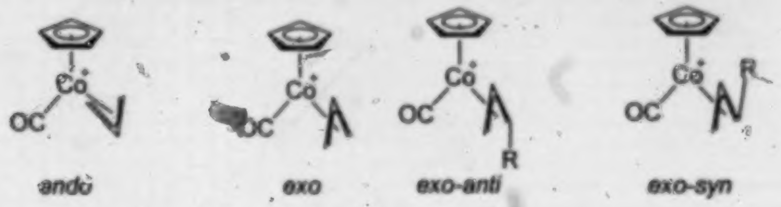
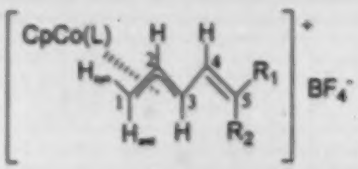
[100] Krivykh, V. V.; Gusev, O.-V.; Petrovskii, P. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *366*, 129 and references within.

Figure 3.1. Stereoisomers of CpCo(allyl)carbonyl complexes



The unsubstituted η^3-pentadienyl complex **95** fits well with the general ^{1}H NMR spectroscopic trends for CpM(allyl)CO complexes compiled by Krivykh across Group 6 to 9 metals (Table 3.3). The chemical shifts of the substituted allyl carbonyl complexes are also consistent with Krivykh's trends.

Table 3.3. Relevant ^{1}H NMR data[a] for



complex	R_1	R_2	L	H_{1anti}	H_{1syn}	H_2	H_3	H_4	H_{5syn}	H_{5anti}	Cp
				chem shift (δ) and coupling constant (Hz)							
95-*syn*	H	H	CO	2.71 ($^2J_{HH}$ = 1.2, $^3J_{HH}$ = 12.3)	4.58 ($^2J_{HH}$ = 1.4, $^3J_{HH}$ = 7.1)	5.92[b]	4.42 ($^3J_{HH}$ = 10.8, 11.4)	6.67 ($^3J_{HH}$ = 10.3, 16.8)	6.04[b]	5.74 ($^2J_{HH}$ = 9.7, $^3J_{HH}$ = 1.8)	5.99
96-*anti*	H	H	CO	2.19[b]	5.07 ($^3J_{HH}$ = 17.0)	5.98[b]	4.92 ($^3J_{HH}$ = 10.1)	6.30 ($^3J_{HH}$ = 10.3, 17.0)	6.08[b]	5.72[b]	5.90
97	Me	H	CO	2.60 ($^2J_{HH}$ = 1.0, $^3J_{HH}$ = 12.2)	4.52[b]	5.89 ($^3J_{HH}$ = 7.1, 12.0)	4.54 ($^3J_{HH}$ = 11.2)	6.47 ($^3J_{HH}$ = 1.5, 10.6, 14.0)	6.63 ($^3J_{HH}$ =7.0, 15.0)	c	5.96
98	Ph	H	CO	2.72 ($^3J_{HH}$ = 12.2)	4.59 ($^2J_{HH}$ = 1.4, $^3J_{HH}$ = 7.1)	6.10 ($^3J_{HH}$ = 7.2, 12.0)	4.74 ($^3J_{HH}$ = 10.8, 10.9)	7.27 ($^3J_{HH}$ = 10.5)	7.32 ($^3J_{HH}$ = 10.5)	c	6.01
99	TMS	H	CO	2.74 ($^2J_{HH}$ = 1.1, $^3J_{HH}$ = 12.3)	4.60 ($^2J_{HH}$ = 1.4, $^3J_{HH}$ = 7.1)	6.02 ($^3J_{HH}$ = 7.0, 12.0)	4.38 ($^3J_{HH}$ = 9.0, 11.6)	6.84[b]	6.82[b]	c	5.98
100	Me	Me	CO	2.58 ($^3J_{HH}$ = 12.2)	4.48 ($^3J_{HH}$ = 6.9)	5.96[b]	4.66 ($^3J_{HH}$ = 11.4)	6.24 ($^3J_{HH}$ = 10.7)	c	c	5.90
103[b,e]	Me	H	AN	2.31	4.52	5.89	4.20	6.32	6.53	c	5.75
104[b,e]	TMS	H	AN	2.52	4.74	6.07	4.02	6.68	6.84	c	5.80

[a] In acetone-d_6. [b] Missing J values due to either overlapping or low-intensity signals. [c] Not applicable due to a non-hydrogen substituent. [d] Chemical shift estimated by GCOSY. AN = acetonitrile. [e] In $CDCl_3$.

Krivykh reported that, in the case of CpCo(crotyl)carbonyl complexes, the *anti*-isomer is the kinetic product while the *syn*-isomer is the thermodynamic product. With heating, a mixture of mostly *anti*-isomer was converted to *syn* (yet never with complete conversion).[100]

In agreement with Krivykh's results, the room temperature reaction (conditions B, **Table 3.1**) leads exclusively to the *syn*-isomer (the thermodynamic product), while, "arrested" reaction conditions (conditions N, Table **3.1**) produces the *anti*-isomer (kinetic product) in a 29 : 71 ratio (*anti*/*syn*). Conditions A (Table **3.1**), which were optimized for the formation of the *syn*-isomer, allow enough time (16 h) for the *anti-syn* conversion, even though the reaction is started at low temperature. While Krivykh's crotyl system required heating to isomerize, the CpCo(η^3-pentadienyl)carbonyl system exhibits a lower kinetic barrier to isomerization to the *syn* isomer, since the conversion occurs at room temperature. The thermodynamic preference for the *syn*-isomer is likely due to a steric effect, since it is seen in both the simple crotyl and vinyl crotyl examples.

Krikykh also discusses the ratio of *endo*/*exo* isomers formed in the protonation/complexation reactions of allyl alcohols and dienes. The allyl ligand exclusively adopts the *exo*-conformation in cobalt, although *endo-exo* mixtures were obtained for other Group 9 metals. A methyl group in the *syn* position also has little impact on the ratio of *endo*/*exo* isomers (exclusively the *exo*-isomer in cobalt). Yet a methyl in the *anti* or central allyl positions greatly affected the ratio of *endo* and *exo* isomers formed. In the case of the 2-methallyl ligand (in all metals studied by Krivykh), only the *endo*-isomer is formed (likely for reasons of steric repulsion between the methyl and the ancillary cyclopentadienyl ligand). Only one isomer is observed in the case of

CpCo, and, since the chemical shift values are within the range observed by Krivykh, it is assumed that the η^3-pentadienyl compounds synthesized in this work are also *exo*-isomers. It is interesting to note that the observations by Krivykh and those detailed herein contradict a theoretical proposal based on MO theory by Eisenstein that the *endo*-isomer is thermodynamically preferred by cationic CpM(allyl)carbonyl complexes of group 9 metals.[101] To determine this with surety using NMR spectroscopy in the η^3-pentadienyl series, one would need to perform NOESY (or TROESY) experiments and measure the NOE between the various protons of the allyl ligand and those of the Cp ring. The various NOE relationships were not pursued, since the goal of the present study was to synthesize η^5-pentadienyl complexes from the cobalt(I) dicarbonyl complex **35**.

It is also interesting to note that Krivykh's CpCo(allyl)carbonyl complexes are relatively stable to standing in acetone. Krivykh accomplishes *endo*/*exo* isomerization in acetone-d_6 over long time periods (e.g., 23 h) and does not report any loss of product to decomposition. Yields of the isomerization experiments were not reported. More will be discussed on this topic in the subsequent section.

X-ray crystal data for η^3-1-trimethylsilylpentadienyl carbonyl complex **99** provided definitive evidence that the proposed structure for this η^3-pentadienyl carbonyl complex is indeed correct and strong evidence that all the reported $[CpCo(\eta^3\text{-pentadienyl})(CO)]^+BF_4^-$ complexes had been successfully synthesized (Figure 3.2). The X-ray crystal data support the stereochemical assignment of *exo* and *syn* for the η^3-pentadienyl ligand. The bond lengths of C_3-C_4 (1.461 Å) and C_4-C_5 (1.341 Å) reflect typical single and double bond lengths respectively, while C_1-C_2 (1.425 Å) and C_2-C_3

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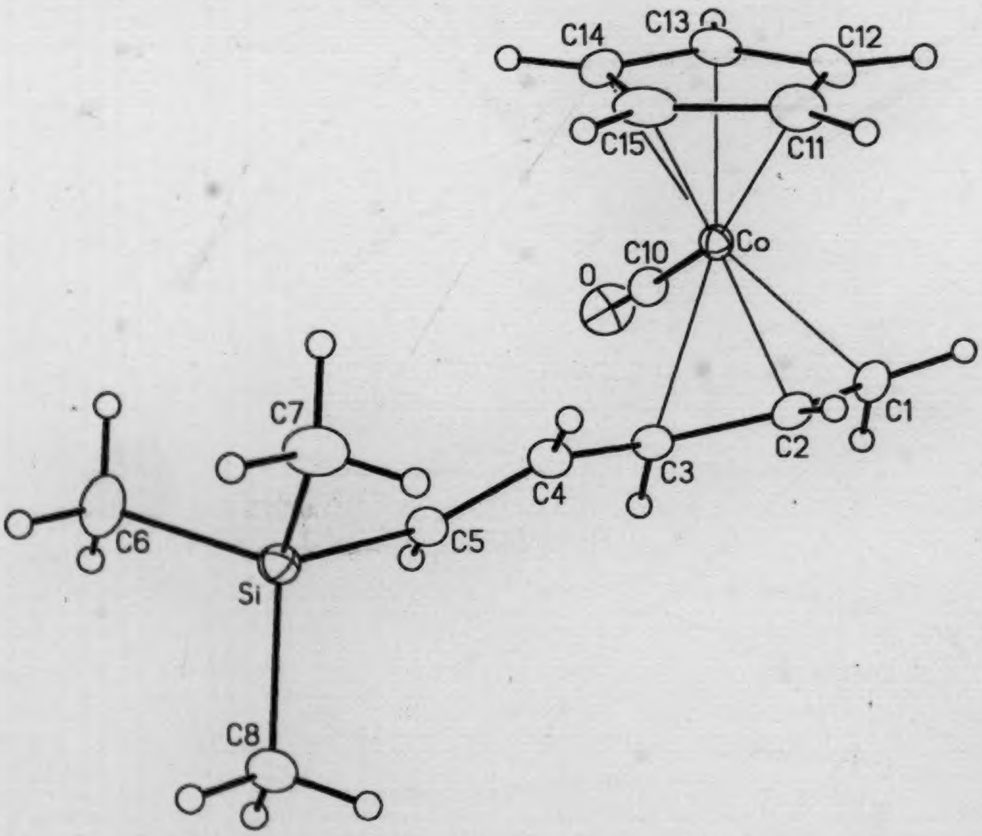
[101] Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

(1.406 Å) reflect typical allyl bond lengths. The torsional bond angle of C_3-C_4-C_5-Si (176.89 deg.) agrees with the *trans* strereochemical assignment.

The characterization of the acetonitrile complexes is, at present, still quite tentative. The acetonitrile complexes were identified by NMR spectroscopy shortly prior to the completion of the present study, and only limited data were available for analysis. The ^{1}H NMR spectral data is similar to that of the carbonyl complexes, yet two key distinctive features are the presence of the acetonitrile peak and the upfield shift of the Cp peak. Otherwise, the identification based upon the pentadienyl chemical shifts would be difficult, since they are quite similar to those of the carbonyl series, as one would expect.

Figure 3.2. ORTEP for Complex **99** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0723

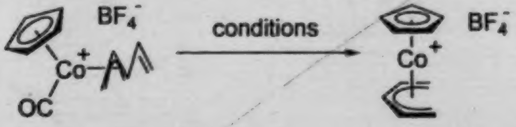


Final Residuals: $R_1 = 0.0339$; $wR_2 = 0.0895$. Data obtained at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.
Selected Bond Distances (Å): Co-C1, 2.090(2); Co-C2, 2.025(2); Co-C3, 2.192(2); C1-C2, 1.425(4); C2-C3, 1.406(3); C3-C4, 1.461(3); C4-C5, 1.341(3).
Selected Bond Angles (deg.): C1-C2-C3, 118.7(2); C2-C3-C4,121.9(2); C3-C4-C5, 123.3(2); Si-C5-C4, 125.18(19).

C. η^5-Pentadienyl complex synthesis

Decarbonylation of the unsubstituted CpCo(*syn*-η^3-pentadienyl)carbonyl complex **95** was first attempted by using Me_3NO. The reaction at room temperature, however, proceeded too vigorously (reaction time was less than one minute) and led to significant decomposition (Entry A, Table 3.4). Even at low temperature (-78 °C), however, the yields were low and conversions incomplete (Entries B, C, Table 3.4). *N*-Methyl-*N*-morpholine oxide, a common alternative amine oxide reagent, provided similar results (Entry D, Table 3.4).

Table 3.4. Decarbonylation of **95** - Optimization Studies



	Solvent	Decarbonylating agent	Temperature (Time)	Yield
A	THF	Me_3NO	RT (5 min)	31%[a]
B	THF	Me_3NO	-30 °C → RT (1 h)	35%[a]
C	THF	Me_3NO	-78 °C → RT (4.5 h)	51%[a]
D	THF	*N*-Me-morpholine-*N*-oxide	-78 °C → RT (4.5 h)	49%[a]
E	THF (<0.01M)	$h\nu$[b]	RT (16 h)	<10%
F	THF	$h\nu$[b]	RT (60 min)	<10%
G	toluene	---	100 °C (3 d)	dec.
H	acetone-d_6	(solvent)	RT (3 d)	[a,c]
I	CH_3CN-d_3	(solvent)	RT (3 d)	30%[a,d]
J	CH_3CN	(solvent)	-50 °C	45%[a,d]
K	CH_2Cl_2 (0.1M)	CH_3CN (1 equiv)	RT (16 h)	51%[a,d]
L	CH_2Cl_2 (0.1M)	CH_3CN (1 equiv)	-50 °C → RT (16 h)	43%[a,d]

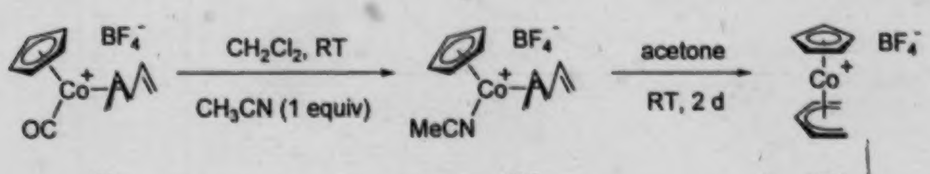
[a] Reaction mixture contains some paramagnetic decomposition product. [b] 450W Hanovia, Ar purge. [c] Yield undetermined. [d] Reaction mixture contains both product and the CpCo(η^3-pentadienyl)(CH_3CN) complex; yield reported corresponds to η^5-product present.

The decarbonylation, in theory at least, was successful, since even a low percentage of η^5-pentadienyl complex **71** was formed. Optimal conditions were then determined for this transformation, which was found to be dependent upon the ratio of *anti/syn* isomers in the initial CpCo(η^3-pentadienyl)carbonyl complex (*vide infra*) (Table **3.4**).

Classical decarbonylation methods – thermal (Entry G, Table **3.4**) and photochemical (Entries E, F, Table **3.4**) – were evaluated using the predominantly *syn*-isomer of the CpCo(η^3-pentadienyl)carbonyl complex, which returned even lower yields and more complex mixtures of products than observed using Me_3NO. Successful conversion to the desired η^5-pentadienyl product was, however, obtained in the absence of reagent and from solvent-assisted decarbonylation (Entries H-L, Table **3.4**). Both acetone and acetonitrile provided significant conversion to η^5-pentadienyl complex **71** without any additives.

An NMR sample of the CpCo(*syn*-η^3-pentadienyl)carbonyl complex was left in acetone-d_6 solution for three days and, after a colour change was observed, NMR spectroscopy revealed the formation of the η^5-pentadienyl complex as well as a significant amount of a decomposition product (Entry H, Table **3.4**). Acetonitrile (as solvent) also effected decarbonylation, however, at a much higher rate of reaction (under one minute at room temperature) than acetone.

The concentration of acetonitrile was then investigated using fewer equivalents (1-2) of acetonitrile (Entries K, L, Table **3.4**) which provided the intermediate acetonitrile complex **102** after a short reaction time. This intermediate was stable under inert atmosphere and for brief periods of time in air and survived column chromatography supports (^{1}H NMR spectroscopy of the acetonitrile complex, however, reflected the presence of paramagnetic material after short exposure to air). Acetonitrile complex **102**, when left exposed to ambient light in acetone-d$_6$, ultimately provided complete conversion to the η^5-pentadienyl complex (Scheme **3.10**).



95 **102** **71**

Scheme 3.10

Optimal reaction conditions (Conditions K, Table **3.4**) for decarbonylation were utilized to achieve the formation of substituted η^5-pentadienyl complexes **72** - **75** from CpCo(η^3-pentadienyl)CO complexes **97** - **100**. Rough yields (35-50%) were obtained for these transformations, and were not further optimized.

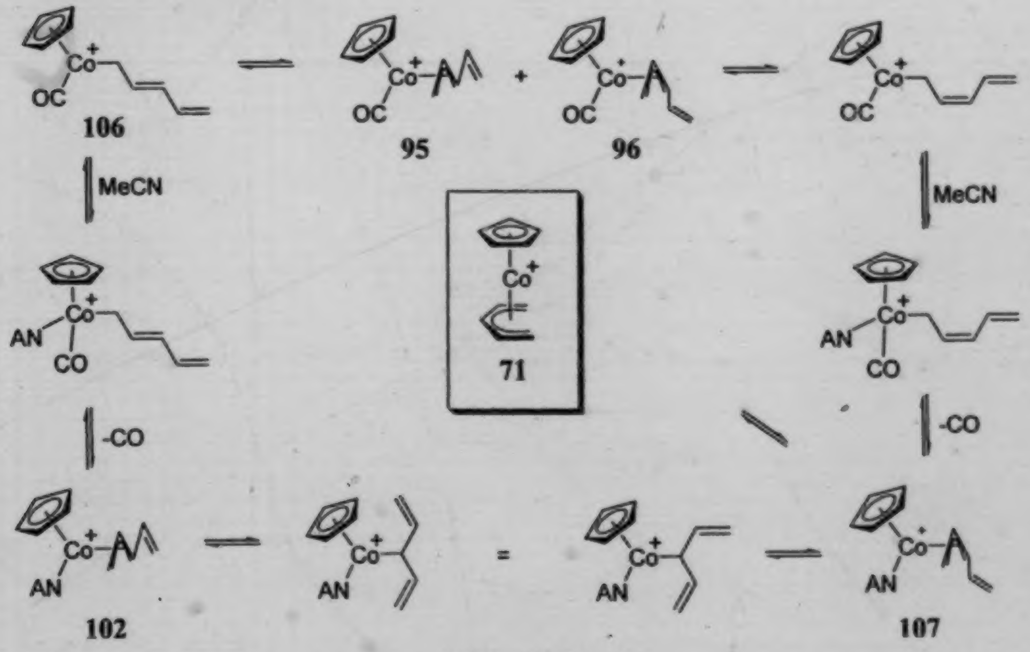
The mixture of *anti* and *syn* isomers was also evaluated for the formation of η^5-pentadienyl complexes. A mixture (29 : 71) of *anti : syn* isomers, left in acetone-d$_6$ for two days, underwent complete decarbonylation. While the process may be assisted photochemically, it is likely that either the acetone or trace water participate in an associative decarbonylation reaction. The acetone or water can intercept the (η^3-pentadienyl)carbonyl complex after an equilibrium isomerization to the η^1-pentadienyl isomer. When the acetone or water remains coordinated, the decarbonylation occurs and the allyl isomerizes back to the η^3-isomer. The process for the isomerization of the *syn*-isomer, as described earlier (Scheme **3.7**) is slow compared with the isomerization of the *anti*-isomer, since the *anti*-isomer is geometrically predisposed to form the η^5-pentadienyl complex, whereas the *syn*-isomer must first isomerize via the η^3-η^1-η^3 reaction manifold. Therefore, it makes sense that, in the presence of acetonitrile, the *syn*-isomer, which is slow to isomerize, forms an intermediate acetonitrile complex, whereas the *anti*-isomer converts directly to the η^5-pentadienyl complex.

D. η^5-Pentadienyl complex characterization

The η^5-pentadienyl complexes **71-75** were characterized by comparison with the products described in Chapter Two. The decarbonylation reactions produced higher proportions of byproducts than obtained from the corresponding bis-ethylene protocol. Similar to Dzwiniel's observations in the CpCo-dienyl manifold, the decarbonylation reaction produces a small amount of cobalticenium by disproportionation.[2] This impurity can not be removed by recrystallization, since it has similar solubility properties to the desired products, and it is equally difficult to remove completely by flash chromatography.

E. Mechanistic discussion

The proposed mechanism for the decarbonylation reactions induced by acetone and acetonitrile involves an associative solvent-assisted pathway (Scheme **3.11**). The η^3-pentadienyl complexes first form a transient acetonitrile complex by η^1-ligand slippage to open a coordination site for the solvent. The η^1-pentadienyl complex is coordinatively unsaturated, leading to incorporation of the solvent. Once formed, the metal is electron-deficient and if the complex is in the presence of a coordinating solvent, the solvent can complex to the metal and satisfy the 18-electron rule. Then, with a more electron-rich metal center, the carbonyl back-bonding will be minimized, making it more easily displaced. The η^1-pentadienyl isomerizes back to η^3 and displaces the carbonyl ligand to give intermediates **102/107**.



Scheme 3.11

The *anti*-η^3-pentadienyl AN complex (**107**) can readily displace the less tightly bound acetonitrile with the pendant vinyl substituent to form the thermodynamically more stable η^5-pentadienyl complex (**71**). The *syn*-η^3-pentadienyl AN complex (**102**), however, requires more time to form the η^5-pentadienyl complex, since it must undergo another isomerization before forming the product. The η^3-pentadienyl ligand must first convert to the central carbon η^1-pentadienyl isomer, rotate the vinyl group about the C_3-

C_4 single bond, and then isomerize back to the *anti*-η^3-pentadienyl complex. Once the η^3-coordinated *anti*-isomer is formed, the process leads to η^5-pentadienyl complex **71**.

The decomposition observed is likely due to homolytic loss of the η^1-pentadienyl complex, rather than isomerizing back to η^3, forming a cobalt(II) intermediate. In the early work of Krivykh and others, η^3-allyl decomposition was observed in solvents such as acetone and acetonitrile. In such systems, however, there is no additional ligand to occupy the open coordination sphere and once the solvent dissociates, the molecule decomposes.

Aviles, as mentioned above, isolated (and even acquired X-ray crystal data) for an aquo complex, which, in the presence of acetonitrile, readily formed an acetonitrile complex.[80] It is possible that the above acetonitrile-assisted decarbonylation of the CpCo(η^3-pentadienyl)carbonyl complex proceeds via a similar mechanistic pathway; however, it is much more likely that the acetone-assisted decarbonylation proceeds via an aquo complex. Acetone is difficult to render rigorously anhydrous, even after vacuum transfer over boric oxide, and the adventitious water is arguably a better ligand than acetone for substitution of the carbonyl ligand. Acetonitrile then more easily exchanges with the water in the aquo complex, forming the observed acetonitrile complex.

This mechanistic proposal (Scheme **3.11**) for the conversion of *syn* and *anti* η^3-pentadienyl carbonyl complexes to η^5-pentadienyl complexes is supported by experimental evidence from studies in the Stryker group with Cp*Co(η^5-pentadienyl) complexes (e.g., **48**) under CO saturation.[3] Witherell observed the formation of a new complex when the Cp*Co(η^5-pentadienyl) complex was saturated in solution with CO at low temperature. The new complex was identified by ^{1}H NMR spectroscopy as the *anti*

η^3-pentadienyl carbonyl complex. The *anti* isomer, as proposed by the mechanistic pathway, is most readily formed from the η^5-pentadienyl complex. The *syn* isomer would require η^3-η^1-η^3 slippage and bond isomerization. Witherell observed thermal instability in the *anti* η^3-pentadienyl carbonyl and spontaneous regeneration of the η^5-pentadienyl complex, and therefore was unable to isolate or purify the *anti* isomer.

III. Conclusion

CpCo(CO)$_2$ (**35**) provides a very convenient starting material for the formation of both η^3-allyl-carbonyl complexes as well as η^5-pentadienyl complexes. The purity of the dicarbonyl starting material is paramount to the success of subsequent reactions, since the most presumed impurities likely compete with the substrate for complexation to the metal. The decarbonylation unfortunately proceeds in only moderate yields and with variable success; however, further development and, in particular, obtaining clean kinetic formation of the *anti*-isomer, is expected to greatly enhance the utility and versatility of this transformation.

Chapter Four: Cationic cobalt(III)-mediated [5+2] cycloaddition reactions: towards the synthesis of functionalized heptadienes

I. Background

A. Cobalt-mediated [3+2+2] cycloaddition reactions in the Stryker group

As mentioned in Chapter One, the Stryker group has demonstrated that Ru and Ir facilitate multi-component cycloaddition reactions for the synthesis of seven-membered rings.[10,102,103,104] These metal systems, however, were relatively expensive (on a stoichiometric scale), limited in scope, and difficult to oxidatively demetallate.[2]

Cobalt was a likely alternative candidate for multicomponent cycloaddition reactivity. Based on work by Rubezhov, *et al.*,[105] Nehl demonstrated that Co(II)allyl complexes yield [3+2] cycloaddition products with various alkynes upon oxidization to Co(III) (Scheme 4.1).[106] Cobalt(III), therefore, was an ideal candidate to explore the mediation of multicomponent cycloaddition reactions. It is interesting to note that Nehl would also have discovered Co-mediated [3+2+2] cycloaddition reactions had he explored different solvents,[10] substrates or less sterically demanding alkynes. It is also possible that the use of crotyl substrates or sterically-demanding alkynes prevented the formation of higher order cycloaddition products, since Etkin demonstrated that crotyl and 1-phenylallyl halides form five-membered ring products with even simple alkynes

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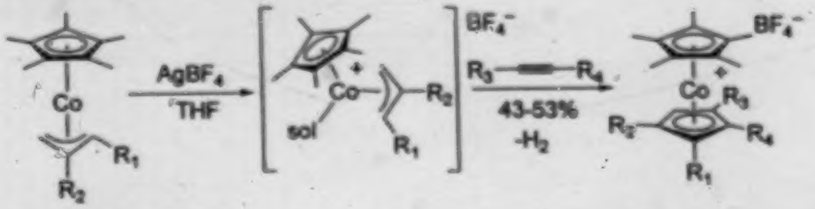
[102] Schweibert, K. E.; Stryker, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 8275.
[103] Dzwiniel, T. L.; Etkin, N.; Stryker, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 10640.
[104] Older, C. M.; McDonald, R.; Stryker, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 14202.
[105] Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349. See refs. within.
[106] Nehl, H. *Chem. Ber.* **1993**, *126*, 1519.

and that cyclopentadienyl complexes are formed even with the unsubstituted allyl halide starting material and phenylacetylene.[2, 107]



R_1, R_2 = H, **109**
R_1 = H, R_2 = Me, **110**

	R_1	R_2	R_3	R_4
111	H	H	Ph	Ph
112	H	H	H	Ph
113	H	H	Me	Me
114	H	Me	Ph	Ph

Scheme 4.1

Schwiebert, Etkin and Dwziniel in the Stryker group demonstrated that cationic cobalt(III)allyl complexes incorporate two equivalents of acetylene in a [3+2+2] cycloaddition reaction to afford a cycloheptadienyl product in moderate to high yields (Scheme 4.2).[10] The [3+2+2] cycloaddition reaction proceeds with substituted alkynes (phenylacetylene and 3,3-dimethyl-1-butyne) and can, in some cases, utilize two different alkynes in sequence. The cycloheptadienyl complexes were then subjected to nucleophilic addition (by both hard and soft nucleophiles) with high stereo- and regioselectivity and subsequent oxidative demetallation to achieve seven-membered carbocycles.

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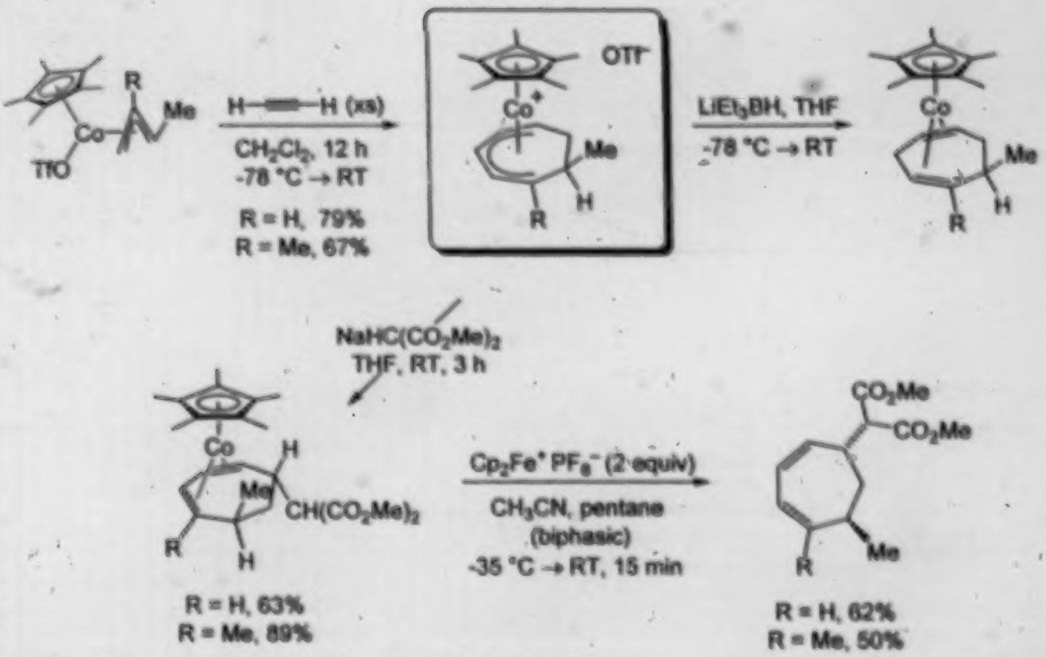
[107] As well, trace water in the THF could have prevented higher order cycloaddition in the Nehl reaction. Spencer has shown that adventitious water encourages cyclization of the pentadienyl ligand. See ref. 35.


R
Me
Co
TfO
H—≡—H (xs)
CH₂Cl₂, 12 h
-78 °C → RT
R = H, 79%
R = Me, 67%
OTf⁻
Co⁺
Me
H
R
LiEt₃BH, THF
-78 °C → RT
Co
Me
H
R
NaHC(CO₂Me)₂
THF, RT, 3 h
Co
H
Me
CH(CO₂Me)₂
R
H
R = H, 63%
R = Me, 89%
Cp₂Fe⁺ PF₆⁻ (2 equiv)
CH₃CN, pentane
(biphasic)
-35 °C → RT, 15 min
CO₂Me
CO₂Me
Me
R
R = H, 62%
R = Me, 50%

Scheme 4.2

In the exploration of the reactivity of Cp*Co(allyl)L complexes (L = halide or OTf), Dzwiniel synthesized Cp analogues of some of the cycloheptadienyl complexes (Scheme 4.3).[2] These [3+2+2] cycloaddition reactions proceeded in fair to moderate yields from either an allyl halide or *in situ* protonation of the diene complex, depending on the substrate.[108] The work with the cyclopentadienyl ancillary ligand in the [3+2+2] cycloaddition reaction demonstrated that the [3+2+2] cycloaddition reaction was tolerant of the differing steric and electronic profile of Cp, yet proceeded most cleanly in the Cp* series.

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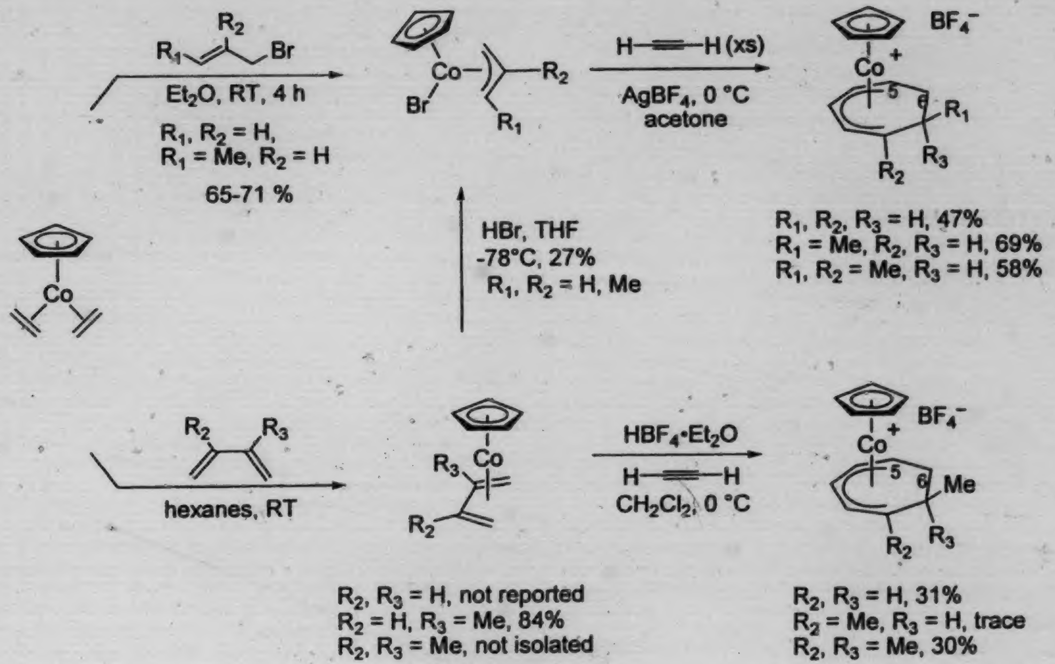
[108] Dzwiniel also synthesized a few examples of bicyclic CpCo(η^5-cycloheptadienyl) complexes, which are not shown since the present discussion focuses primarily on monocyclic heptadienyl complexes. See ref. 2 for further details.


R$_2$
R$_1$
Br
Et$_2$O, RT, 4 h
R$_1$, R$_2$ = H,
R$_1$ = Me, R$_2$ = H
65-71 %
Co
Br
R$_2$
R$_1$
H—≡—H (xs)
AgBF$_4$, 0 °C
acetone
BF$_4^-$
Co$^+$
5
6
R$_1$
R$_3$
R$_2$
R$_1$, R$_2$, R$_3$ = H, 47%
R$_1$ = Me, R$_2$, R$_3$ = H, 69%
R$_1$, R$_2$ = Me, R$_3$ = H, 58%
HBr, THF
-78°C, 27%
R$_1$, R$_2$ = H, Me
Co
R$_2$
R$_3$
hexanes, RT
R$_3$
Co
R$_2$
HBF$_4$•Et$_2$O
H—≡—H
CH$_2$Cl$_2$, 0 °C
BF$_4^-$
Co$^+$
5
6
Me
R$_2$
R$_3$
R$_2$, R$_3$ = H, not reported
R$_2$ = H, R$_3$ = Me, 84%
R$_2$, R$_3$ = Me, not isolated
R$_2$, R$_3$ = H, 31%
R$_2$ = Me, R$_3$ = H, trace
R$_2$, R$_3$ = Me, 30%

Scheme 4.3[2]

In the course of studying the scope of the Cp*Co-mediated [3+2+2] cycloaddition reaction, Etkin and Dzwiniel found the use of disubstituted alkynes provided access to unexpected substitution patterns on the cycloheptadienyl ligand, a complex reaction process that proceeds via carbon-carbon bond activation.[103] Spencer had previously demonstrated that agostic Cp*Co(η^3-cyclopentenyl) complexes (prepared by different means) convert thermally to the open pentadienyl complex by carbon-carbon bond activation (Scheme **2.5**);[35,36] Dzwiniel also demonstrated that similar agostic cyclopentenyl complexes were likely reactive intermediates in the carbon-carbon bond activation reactions to form cycloheptadienyl products (Scheme **4.4**).[109] Even though subsequent evidence indicates that the [5+2] cycloaddition reaction is not on the reaction surface of the anomalous [3+2+2] cycloaddition reaction, the possibility of developing a novel thermal [5+2] pentadienyl/alkyne cycloaddition reaction was of fundamental and synthetic interest, and therefore evaluated as another new synthesis of cycloheptadienes.

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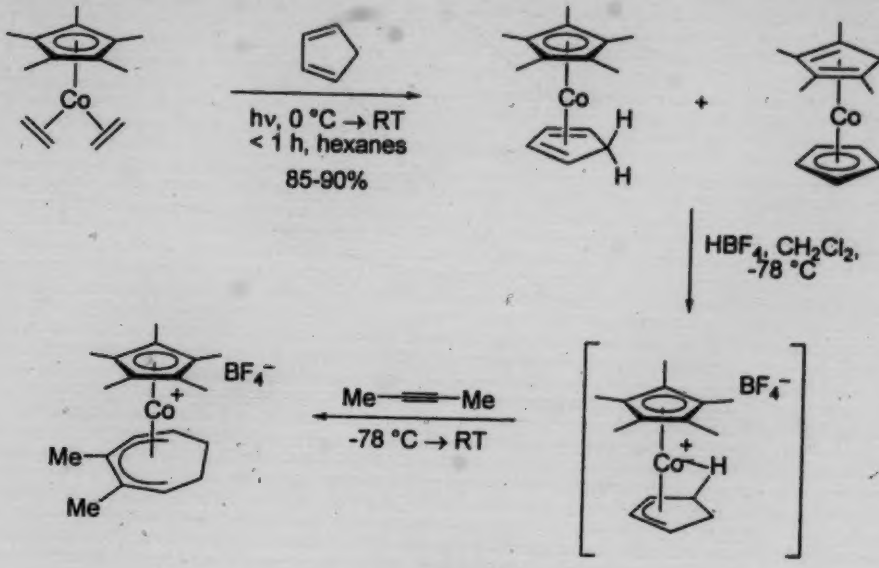
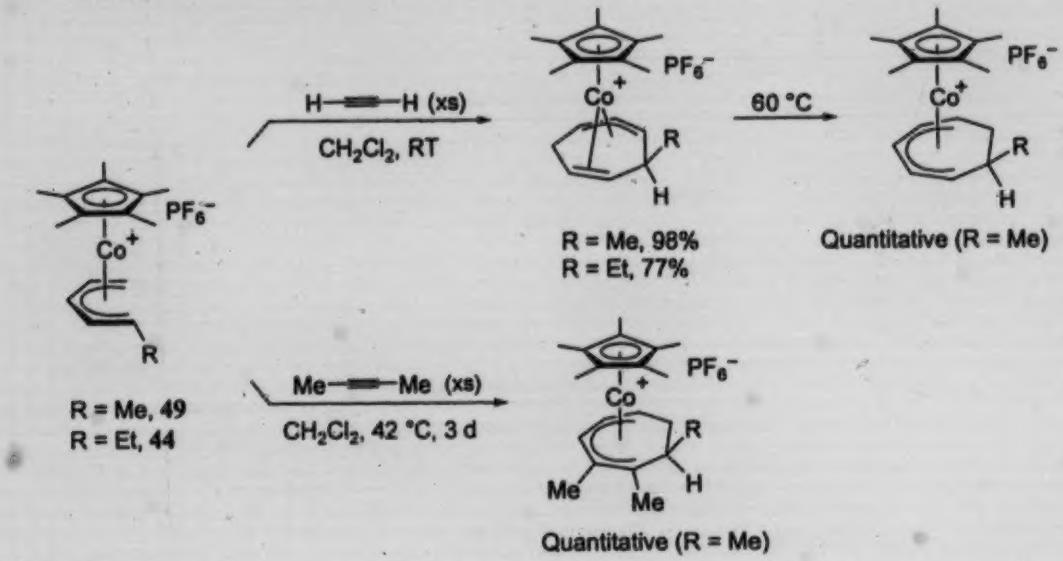
[109] Dzwiniel, T.L.; Stryker, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 9184.



Scheme 4.4

B. Cp*Co [5+2] cycloaddition reactions: scope and limitations

The [5+2] cycloaddition reaction was successfully demonstrated using the Cp*Co system, beginning with either 1-methylpentadienyl complex **49** or 1-ethylpentadienyl complex **44** (Scheme **4.5**). In both cases, the reaction with acetylene proceeds stereoselectively to yield one air- and moisture-stable η^3,η^2-cycloheptadienyl complex, which resists isomerization in the solid state at room temperature. In solution, isomerization to the fully-conjugated product proceeds slowly and was promoted thermally with the addition of minimal heat. Complex **49** also yielded a trisubstituted-cycloheptadienyl complex upon reaction with 2-butyne. The Cp*Co [5+2] cycloaddition reaction of **49** with 2-butyne required minor heating to initiate and thus gave complete conversion to the fully conjugated product. The η^3,η^2-cycloheptadienyl complex was observed but could not be isolated.


H—≡—H (xs)
CH₂Cl₂, RT
PF₆⁻
Co⁺
R
H
R = Me, 98%
R = Et, 77%
60 °C
Quantitative (R = Me)
R = Me, 49
R = Et, 44
Me—≡—Me (xs)
CH₂Cl₂, 42 °C, 3 d
Me
Me
Quantitative (R = Me)

Scheme 4.5

The Cp*Co [5+2] cycloaddition reaction also proceeded with other 1-alkylpentadienyl complexes, such as 1-phenylpentadienyl complex **115** (Scheme **4.6**).[110] Complex **115** is more reactive towards alkynes than **49**; reaction mixtures from the acetylene cycloaddition reaction contain both the η^3,η^2-cycloheptadienyl product and the fully-conjugated η^5-product. Similar to **49**, the η^3,η^2-cycloheptadienyl product of **115** and acetylene can be isomerized to the fully-conjugated product at slightly elevated temperatures.

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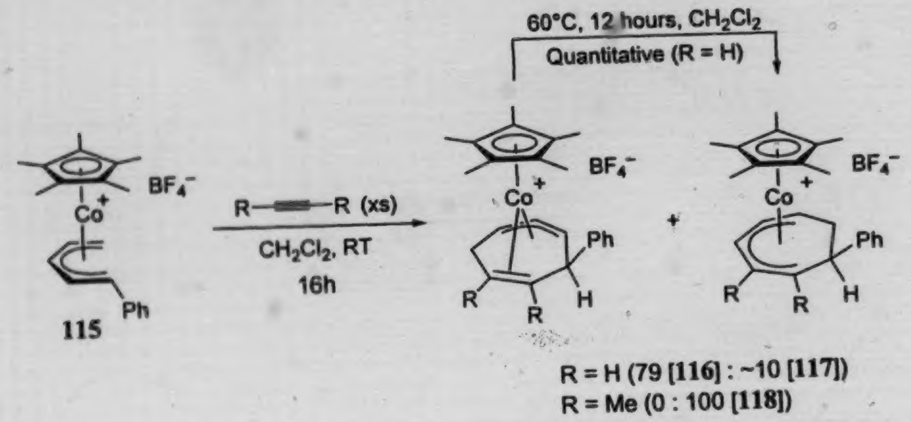
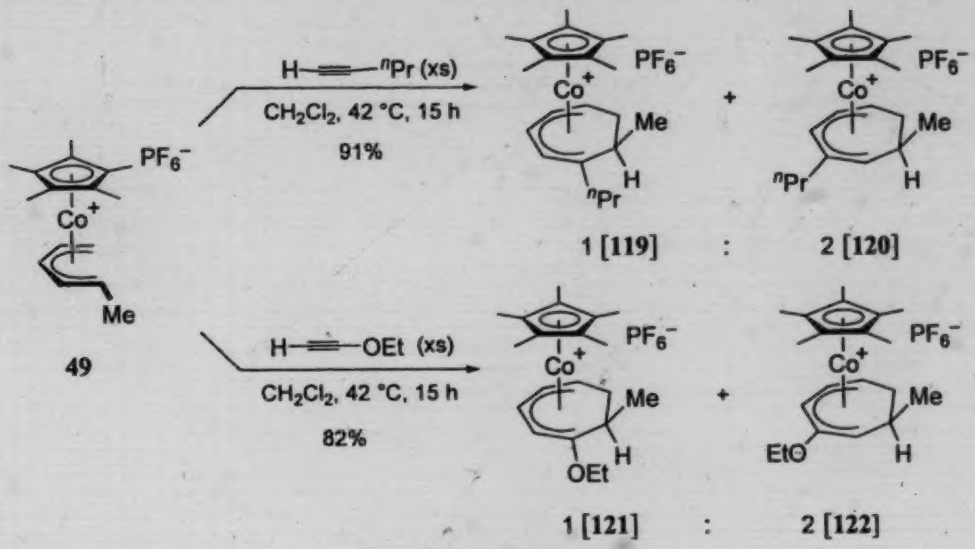
[110] All Cp*Co [5+2] cycloaddition reactions presented herein were performed by R. D. Witherell, with the exception of the examples with phenylpentadienyl complex **115**, which were performed by K. E. O. Ylijoki.


60°C, 12 hours, CH2Cl2
Quantitative (R = H)
BF4−
Co+
Ph
115
R—≡—R (xs)
CH2Cl2, RT
16h
BF4−
Co+
Ph
R
R
H
+
BF4−
Co+
Ph
R
R
H
R = H (79 [116] : ~10 [117])
R = Me (0 : 100 [118])

Scheme 4.6

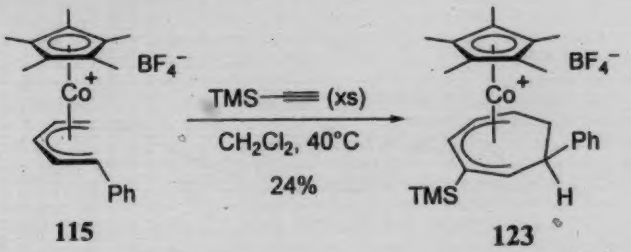
The scope of the Cp*Co [5+2] cycloaddition reaction, however, was limited to 1-alkyl-substituted-pentadienyl complexes. The [5+2] cycloaddition reaction with the unsubstituted pentadienyl complex as well as 2-alkyl-substituted pentadienyl complexes yielded only decomposition products or gave no reaction, even at elevated temperatures (>100 °C).

The regioselectivity of the [5+2] cycloaddition reaction was then evaluated for unsymmetrical alkynes. In reaction of the 1-methylpentadienyl complex **49**, the [5+2] cycloaddition reaction provided no significant regiocontrol (Scheme **4.7**). The lack of regioselectivity in the case of two isosteric alkynes with differing electronic profiles – 1-pentyne and ethoxyacetylene – demonstrates that electronic effects likely do not affect the regioselectivity of the [5+2] cycloaddition reaction, since there was no significant difference in the ratio of the regioisomers formed by the two alkynes.


H—≡—ⁿPr (xs)
CH₂Cl₂, 42 °C, 15 h
91%
H—≡—OEt (xs)
CH₂Cl₂, 42 °C, 15 h
82%
PF₆⁻
Co⁺
Me
H
ⁿPr
OEt
EtO
49
1 [119] : 2 [120]
1 [121] : 2 [122]

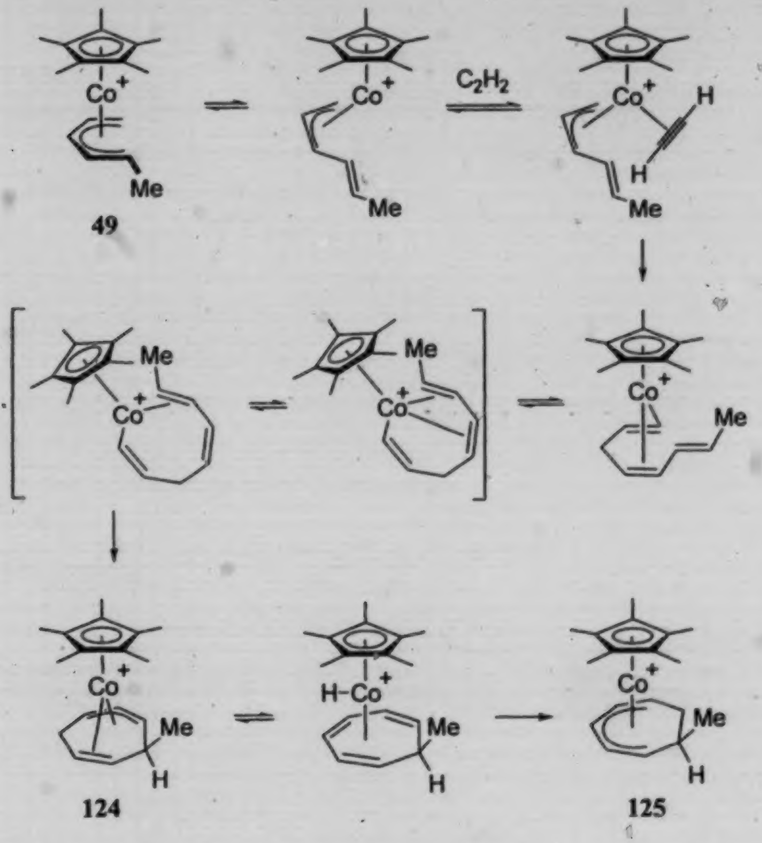
Scheme 4.7

In the case of complex **115**, there was a degree of regioselectivity in the [5+2] cycloaddition reaction, although the reaction itself proceeded in low yield (Eq **4.2**). Only one cycloheptadienyl complex was obtained from cycloaddition with trimethylsilylacetylene – the fully-conjugated product expected based on steric repulsion between the two bulky substituents. The regioselectivity of the Cp*Co [5+2] cycloaddition reaction, therefore, seems to be governed primarily by the steric repulsion among the substrate substituents. In the case of complex **49**, the steric repulsion between the alkyne substituent and the terminal methyl group is clearly not as significant as that between the phenyl and trimethylsilyl groups.


TMS—≡ (xs)
CH₂Cl₂, 40°C
24%
BF₄⁻
Co⁺
Ph
TMS
H
115
123

Eq 4.2

Based on the reactivity observed, a mechanism was proposed for the [5+2] cycloaddition reaction of complex **49** and acetylene (Scheme **4.9**). The η^5-pentadienyl ligand in **49** initially isomerizes to an η^3-pentadienyl ligand, dissociating the pendant vinyl group in order to open a coordination site for the alkyne. The alkyne then coordinates, inserts, and, after isomerization, carbometallates intramolecularly to form the η^3,η^2-cycloheptadienyl complex **124**. Subsequently, a β-hydride is slowly abstracted from the methylene by the Co and added to any available site on the transient triene complex until thermodynamically-favoured η^5-cycloheptadienyl complex **125** is formed.



Scheme 4.9

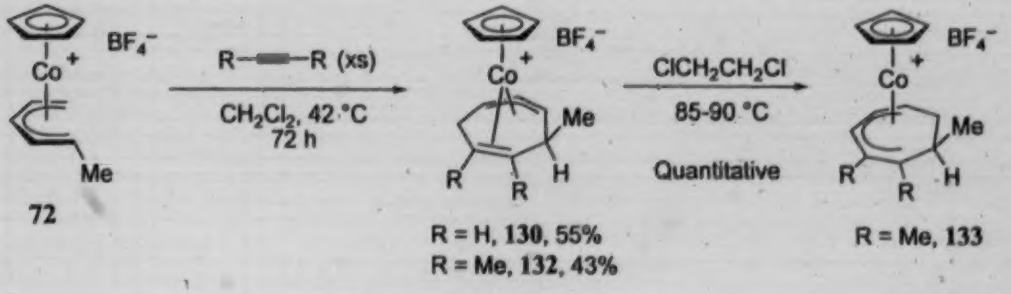
C. Project Goal

The goal of the third part of this project was to explore and expand the scope of the [5+2] pentadienyl/alkyne cycloaddition reaction discovered using the pentamethylcyclopentadienyl ancillary ligand system. As mentioned, this reaction proceeds stereoselectively in good to excellent yields, yet with poor regioselectivity for unsymmetrical alkynes and with limited scope in general. The goal of the cyclopentadienyl ancillary ligand exploration was to determine the scope and limitations of the reactivity and to determine the ligand (steric and electronic) effects on the reactivity and regioselectivity.

II. Results and Discussion

A. η^3,η^2- and η^5-Cycloheptadienyl complexes

The 1-methylpentadienyl complex **72** was chosen as the first candidate to investigate for [5+2] cycloaddition reactivity. The Cp* analogue (**49**) is highly reactive towards [5+2] cycloaddition reactions with alkynes and complex **72** was readily available, as discussed (Chapter Two).


BF$_4^-$
Co$^+$
Me
72
R—≡—R (xs)
CH$_2$Cl$_2$, 42 °C
72 h
BF$_4^-$
Co$^+$
Me
R
R
H
R = H, 130, 55%
R = Me, 132, 43%
ClCH$_2$CH$_2$Cl
85-90 °C
Quantitative
BF$_4^-$
Co$^+$
Me
R
R
H
R = Me, 133

Scheme 4.10

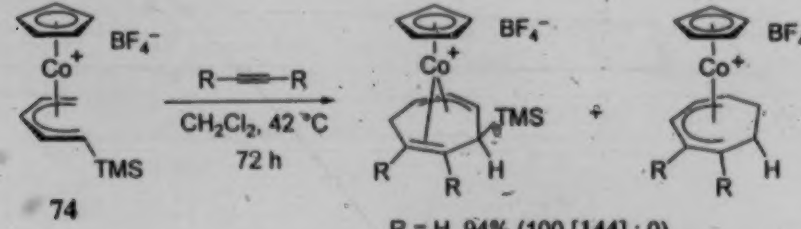
Reaction conditions similar to the Cp* system provided moderate yields of cycloheptadienyl products from the cycloaddition reaction of complex **72** and either acetylene or 2-butyne (Scheme **4.10**). These reactions proceed in dichloromethane (anhydrous but not degassed) at slightly elevated temperatures (40-45 °C) over 72 hours using an excess of alkyne. A ten-fold excess of alkyne was typically used to ensure reaction completion; however, the cycloaddition reactions could be accomplished with as few as two equivalents of alkyne. For novel or costly alkyne substrates, the reactivity with fewer alkyne equivalents is of greater significance.

Like in the Cp* system, the cyclopentadienyl cobalt(III) η^5-pentadienyl complexes formed "interrupted" η^3,η^2-cycloheptadienyl complexes in the [5+2] cycloaddition reactions with acetylene. While the Cp* analogues very slowly converted to the fully-conjugated η^5-isomers in solution at room temperature, the Cp complexes were completely stable and resistant to isomerization at room temperature. In the Cp system, conversion to the thermodynamically-favoured η^5-cycloheptadienyl isomer required elevated (80-90 °C) temperatures maintained for a 24 hour time period. As proposed in the mechanism for the Cp* [5+2] cycloaddition reaction (Scheme **4.9**), this observation is consistent with the proposal that the η^3,η^2-isomer is on the reaction pathway to the η^5-isomer. In both cases (Cp* and Cp), this η^3,η^2-isomer is an isolable intermediate for at least some alkynes.

The first significant difference in reactivity between the Cp and Cp* ligand system was observed in the reaction with 2-butyne. While Cp* complex **49** exclusively provides the thermodynamically-favoured η^5-cycloheptadienyl complex upon minimal heating, the reaction with the corresponding Cp complex **72** halts, providing exclusive formation of the kinetic, η^3,η^2-coordinated product (Scheme **4.10**). The exclusive formation of the kinetic product can be utilized synthetically to provide access to a greater breadth of η^3,η^2-cycloheptadienyl complexes (and eventually 1,4-cycloheptadienes) than one could access by using the Cp* ligand.

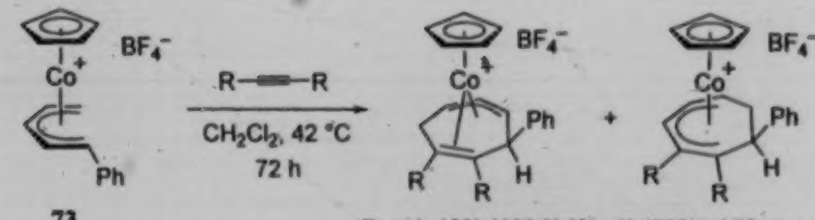
The [5+2] cycloaddition reaction was also evaluated for the reaction of 1-methylpentadienyl complex **72** and diphenylacetylene, which required minimal heating (42 °C) over a 48 hour reaction period. This resulted in a very poor yield and a mixture of products. By careful analysis of the 2D ^{1}H GCOSY spectrum (*vide infra*), the majority of the reaction mixture was tentatively identified as the expected η^3,η^2-cycloheptadienyl isomer.

Other 1-substituted η^5-pentadienyl complexes of even greater steric profile were evaluated for reactivity in the [5+2] cycloaddition reaction (Schemes **4.11** and **4.12**). Both 1-phenyl- and 1-trimethylsilyl-η^5-pentadienyl complexes **73** and **74**, respectively, formed cycloheptadienyl products in good to excellent yields. Trimethylsilyl complex **74** provided the expected η^3,η^2-cycloheptadienyl products upon reaction with both acetylene and 2-butyne (Scheme **4.11**); phenyl-substituted complex **73**, however, was more reactive under the same conditions and led to a mixture of η^3,η^2- and η^5-isomers, still heavily weighted toward the kinetic product (Scheme **4.12**). This latter observation is consistent with the greater reactivity and instability of complex **73** (as discussed in Chapter Two) as well as the increased reactivity of the Cp* analogue towards [5+2] cycloaddition reactions. It is also important to note that the minor fully conjugated product was desilylated in the reaction of complex **74** with 2-butyne. The phenomenon of thermal desilylation during cycloaddition reactions has been observed previously in the Stryker group and elsewhere.[111,112]


BF$_4^-$
Co$^+$
R—≡—R
CH$_2$Cl$_2$, 42 °C
72 h
TMS
74
BF$_4^-$
Co$^+$
TMS
R
R
H
+
BF$_4^-$
Co$^+$
R
R
H

R = H, 94% (100 [**144**] : 0)
R = Me, 90% (95 [**146**] : 5 [**129**])

Scheme 4.11


BF$_4^-$
Co$^+$
R—≡—R
CH$_2$Cl$_2$, 42 °C
72 h
Ph
BF$_4^-$
Co$^+$
Ph
R
R
H
+
BF$_4^-$
Co$^+$
Ph
R
R
H

73

R = H, 12% (100 [**140**] : 0) (57% of **73** recovered)
R = Me, 63% (87 [**142**] : 13 [**143**])

Scheme 4.12

The unsubstituted η^5-pentadienyl complex **71** was also subjected to cycloaddition reaction conditions. The Cp* analogue, as discussed, does not react cleanly to form cycloheptadienyl complexes. While complex **71** proved less reactive than the methyl-substituted complex **72** toward cycloaddition reactions, it nonetheless provides cycloheptadienyl complexes in modest yields (Scheme **4.13**). In the reaction with acetylene, complex **71** yields a mixture of the η^3,η^2- and η^5 isomers (ca. 50% conversion)

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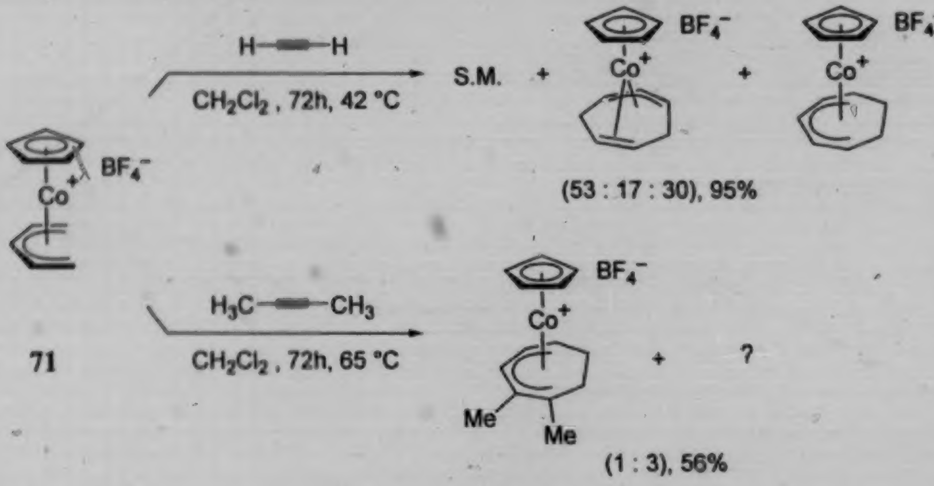
[111] Older, C. M. Ph.D. Thesis, University of Alberta, Edmonton, Alberta, Canada, 2000.
[112] Sánchez-Castro, M. E.; Ramirez-Monroy, A.; Paz-Sandoval, M. A. *Organometallics* **2005**, *24*, 2875.

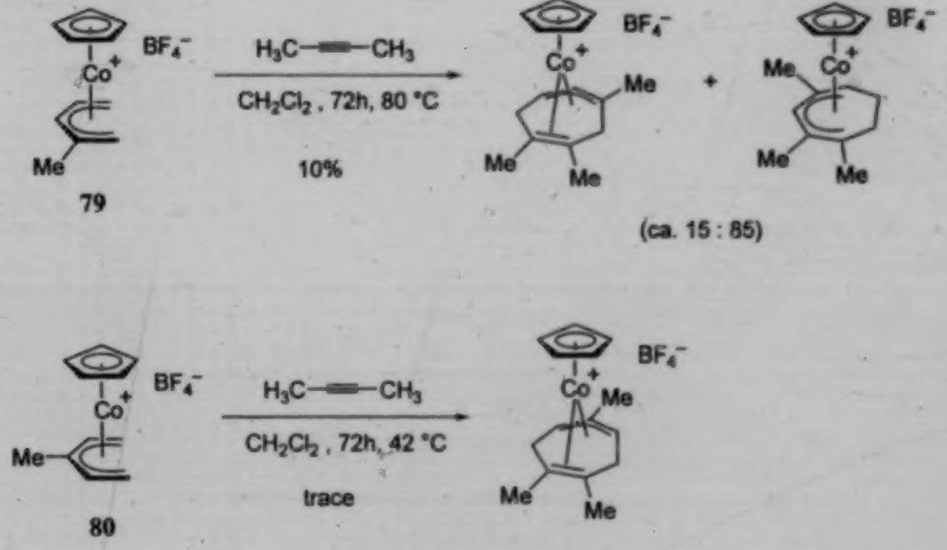
after minimal heating over 72 h. The identity of the fully-conjugated cycloheptadienyl isomer was confirmed by comparison with Dzwiniel's spectroscopic data (*vide infra*).[2] With 2-butyne, a mixture (2 : 3) of the η^3,η^2-cycloheptadienyl isomer and an unidentified byproduct is obtained in moderate yield at 40-45 °C for 72 h. At slightly elevated temperatures (60-65 °C), the reaction with 2-butyne gives a mixture of the unidentified byproduct and the fully conjugated cycloheptadienyl product in a 3 : 1 ratio after 72 h.

While the yields of [5+2] cycloaddition reactions are still relatively low, the reactivity of the unsubstituted pentadienyl complex **71** expands the scope of the reaction in comparison to the Cp* ligand system. Even though the synthetic utility of the [5+2] cycloaddition reaction with complex **71** is limited, the improved reactivity of the complex raises fundamental questions about the reactivity of the cobalt system towards [5+2] cycloaddition reactions, for which there is only currently speculation.

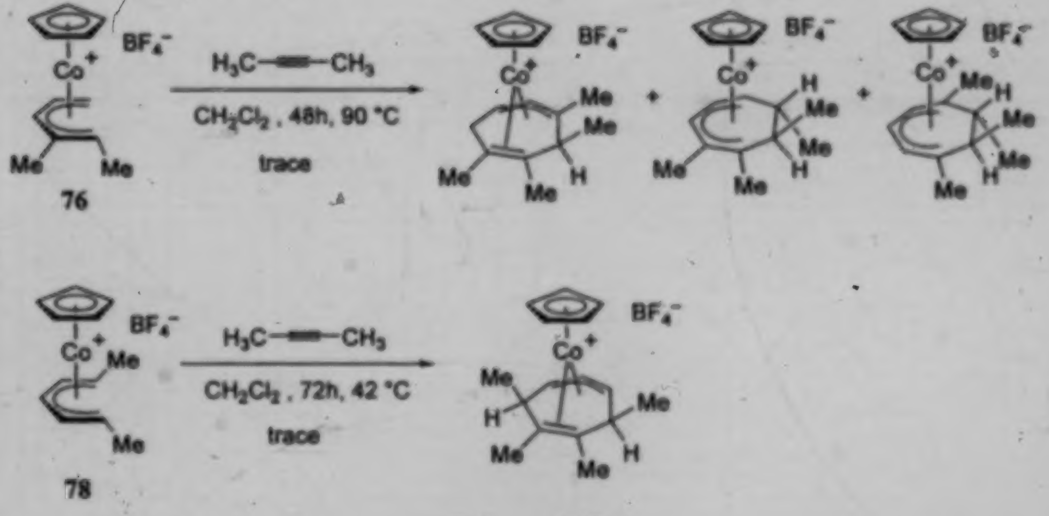


Scheme 4.13

In addition to the unsubstituted and 1-substituted η^5-pentadienyl complexes, various other mono- and disubstituted η^5-pentadienyl complexes were evaluated for reactivity in [5+2] cycloaddition reactions (Schemes **4.14** and **4.15**, respectively). Both heptadienyl complex **78** and 3-methylpentadienyl complex **80** react with 2-butyne under the standard conditions to give the tentatively assigned η^3,η^2-cycloheptadienyl product, albeit in very low yields. 3-Methylhexadienyl complex **76** and 2-methylpentadienyl complex **79** react with 2-butyne, but require elevated temperature (80-90 °C) to induce a reaction. Isomeric mixtures of η^3,η^2- and η^5-cycloheptadienyl complexes were obtained, again in very low yields. Due to this poor reactivity, these substrates were not further evaluated.

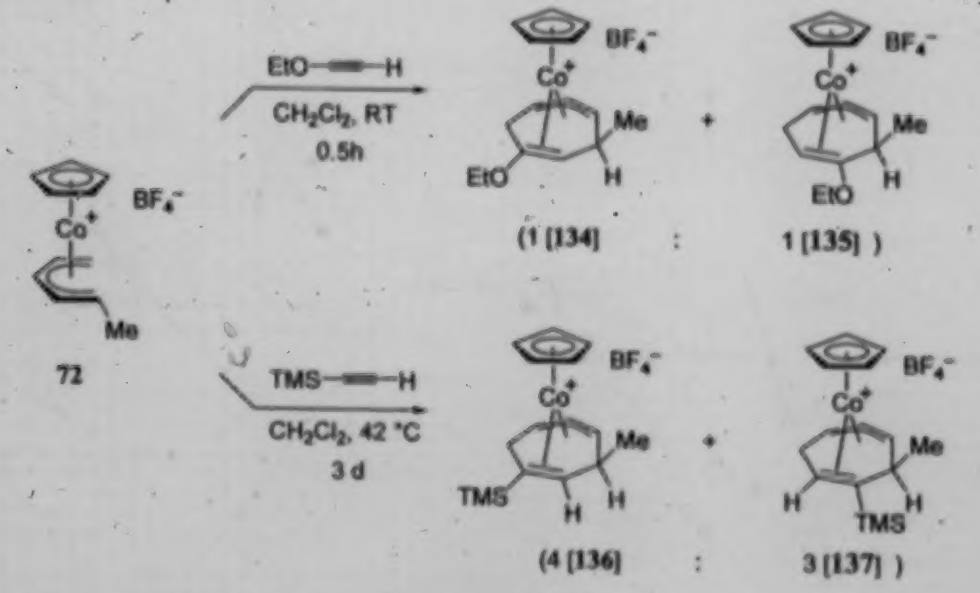

BF₄⁻
Co⁺
Me
79
H₃C—≡—CH₃
CH₂Cl₂, 72h, 80 °C
10%
BF₄⁻
Co⁺
Me
Me
Me
+
BF₄⁻
Co⁺
Me
Me
Me
(ca. 15 : 85)
BF₄⁻
Co⁺
Me
80
H₃C—≡—CH₃
CH₂Cl₂, 72h, 42 °C
trace
BF₄⁻
Co⁺
Me
Me
Me

Scheme 4.14



Scheme 4.15

The final exploration addressed the regioselectivity of the Cp system upon reaction with unsymmetrical alkynes. Since 1-methylpentadienyl complex **72** reacts cleanly with symmetrical alkynes and presented a moderate steric bias upon reaction with some unsymmetrical alkynes, the reactivity of the 1-methylpentadienyl complex was evaluated first. Upon addition of excess ethoxyacetylene or trimethylsilylacetylene, complex **72** reacts but does not exhibit any regioselectivity in the [5+2] cycloaddition reaction (Scheme **4.16**). While the reaction of complex **72** with tri-isopropylsilylacetylene under the standard cycloaddition reaction conditions returned only starting material, phenyl-substituted complex **73** does react but forms isomeric mixtures containing additional byproducts, all in very low yields. The only reaction that displays a degree of regioselectivity is the cycloaddition of trimethylsilyl complex **74** and phenylacetylene. This variation of the Cp* reaction of the 1-phenylpentadienyl complex with TMS-acetylene yielded a majority of the 1,3-substituted *η*^{3},*η*^{2}-cycloheptadienyl product, along with numerous other decomposition products, from which the desired product could not be separated.

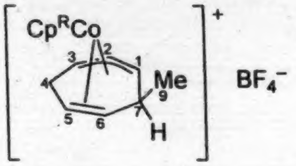


Scheme 4.16

B. η^3,η^2- and η^5-Cycloheptadienyl complexes: characterization

The physical and spectroscopic properties of the cationic CpCo(cycloheptadienyl) complexes are very similar to the Cp*Co(cycloheptadienyl) complexes. All of the CpCo(cycloheptadienyl) spectroscopic data (chemical shifts, coupling constants) is consistent with those of the Cp* ligand system, for which rigorous spectroscopic analysis as well as numerous X-ray crystal structures are available to support structural assignments (Table 4.1).[11] The red to dark-red Co(III) cycloheptadienyl complexes are stable to air and moisture.

Table 4.1. Comparison of relevant ^1H NMR data[a] of a cationic Cp* and CpCo(cycloheptadienyl) complex



	Cp*	Cp
H_1	3.55 (7.6, 3.7)	4.70 (7.3, 3.7)
H_2	3.22 (7.6)	4.01 (7.5)
H_3	3.85 (7.6, 8.5, 4.2)	5.10[b]
H_{4endo}	3.06 (14.2, 8.5, 7.9)	3.14[b] (14)
H_{4exo}	2.17 (14.2, 4.7, 4.7)	2.28[b] (14)
H_5	2.71 (6.6, 8.6, 4.7)	3.73[b] (7.0)
H_6	2.35 (6.6, 5.0)	3.39[b] (5.4)
H_{7exo}	2.40[b]	2.70 (13.5, 5.8)

[a] In ppm (Hz). [b] Missing *J* values due to either overlapping or low-intensity signals.

The cationic CpCo(cycloheptadienyl) complexes were fully characterized by ^1H and ^{13}C NMR and IR spectroscopy, mass spectrometry and elemental analysis (where possible). Samples were purified for NMR spectroscopy using silica gel column chromatography, yet analytically pure material required recrystallization using pin-hole diffusion (dichloromethane and diethyl ether).[113] X-ray crystal data was obtained for η^3,η^2-*endo*-7-methylcycloheptadienyl complex **130** after recrystallization and provides unambiguous identification of the η^3,η^2-isomer. The identity of the unsubstituted η^5-

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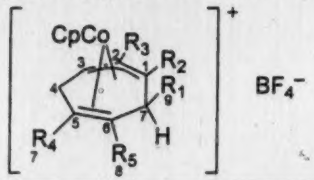
[113] While the starting pentadienyl complexes could be separated from the desired cycloheptadienyl products (the starting material was more polar and eluted more slowly), the two product isomers could not be separated by column chromatography.

cycloheptadienyl complex **127** was confirmed by comparison with previously published data by Dzwiniel, as mentioned above.[2]

Tables **4.2** and **4.3** summarize relevant ^{1}H NMR data for selected η^3,η^2- and η^5-cycloheptadienyl complexes. It is interesting to note that the most upfield protons of CpCo(η^5-cycloheptadienyl) complexes appear as much as 2 ppm further upfield than the respective alkyl protons of the CpCo(η^3,η^2-cycloheptadienyl) complexes. These findings are consistent with Dzwiniel's determination that the saturated C_6 and C_7 atoms in the Cp* cycloheptadienyl system are not planar with the rest of the fully conjugated ligand (Figure **4.1**).[2] With the absence of the sterically bulky methyls of the Cp* ligand, the methylene groups of the cycloheptadienyl ligand can torque to minimize eclipsing interactions between the vicinal protons (and substituents) on the two carbons and the C_7 *endo*-substituent is able to rotate upwards towards the smaller ancillary ligand.

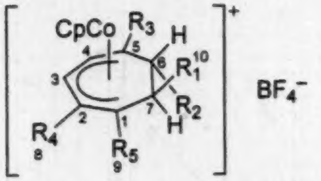
Table 4.2. Relevant ^{1}H NMR data[a] for



						chem shift (δ) and coupling constant (Hz)									
complex	R_1	R_2	R_3	R_4	R_5	H_1	H_2	H_3	H_{4endo}	H_{4exo}	H_5	H_6	H_{7endo}	H_{7exo}	Cp
126[b]	H	H	H	H	H	5.10	4.08	5.10	3.15	2.30	3.85	3.85	3.15	2.30	
128	H	H	H	Me	Me	5.40 (ddd)	4.20 (t)	5.40 (ddd)	3.11 (dd)	2.67 (dd)	c	c	3.11 (dd)	2.67 (dd)	5.45
130[d]	Me	H	H	H	H	4.70 (*J* = 3.7, 7.3)	4.01 (*J* = 7.5)	5.10 (ddd)	3.14 (dd)	2.28	3.73	3.39 (*J* = 5.4)	c	2.55 (dq)	5.75
132[d]	Me	H	H	Me	Me	4.86 (*J* = 4.5, 6.7)	4.14 (*J* = 7.3)	5.32 (m)	3.12 (*J* = 9.3, 14.2)	2.63 (*J* = 4.6, 14.0)	c	c	c	2.70 (*J* = 13.5, 5.8)	5.48
136[b]	Me	H	H	TMS	H	4.63	4.15	5.30	3.12	2.20	c	3.61	c	2.58	5.70
140[e]	Ph	H	H	H	H	4.95 (dd)	4.15 (J = 7.0)	5.18 (ddd)	3.44 (dd)	c	3.57	3.89	c	2.34 (dd)	5.70
142	Ph	H	H	Me	Me	3.81	4.32	5.44	3.27	2.94	c	c	c	1.78	5.60
144	TMS	H	H	H	H	4. 95	4.10	5.05	3.10	2.40	3.90	3.62	c	1.88	5.68
146[e]	TMS	H	H	Me	Me	5.05 (*J* =5.9, 6.8)	4.29 (*J* = 7.1, 6.1)	5.43	3.18 (*J* = 9.5, 14.2)	2.68 (*J* = 3.4, 14.4)	c	c	c	1.90 (*J* = 5.9)	5.37
149[b]	Me	H	H//Me	Me	Me	4.78	4.12	4.78	c	2.77	c	c	c	2.77	5.90

[a] In acetone-d_6. [b] Missing *J* values due to either overlapping or low-intensity signals. [c] Not applicable due to a non-hydrogen substituent. [d] *J* values from sample in $CDCl_3$. [e] In $CDCl_3$.

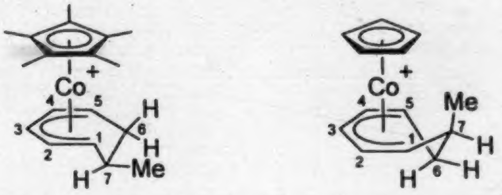
Table 4.3. Relevant ^{1}H NMR data[a] for



						chem shift (δ) and coupling constant (Hz)									
complex	R_1	R_2	R_3	R_4	R_5	H_1	H_2	H_3	H_4	H_5	H_{6exo}	H_{6endo}	H_{7endo}	H_{7exo}	Cp
127	H	H	H	H	H	5.60	5.80	7.41	5.80	5.60	1.25	2.49	2.49	1.25	5.78
129	H	H	H	Me	Me	c	c	7.17 ($^3J_{HH}$ = 7.3)	5.23 (J = 9.1, 7.5, 1.5)	5.65 (m)	3.19 ($^2J_{HH}$ = 19.9, $^3J_{HH}$ = 11.7, 7.7, 3.5)	2.05 (J = 1.5)	1.50 (J = 12.3, 7.7 1.5)	0.32 (J = 12.4, 5.3)	5.57
133[d]	Me	H	H	Me	Me	c	c	7.21 ($^3J_{HH}$ = 7.2)	5.21 ($^3J_{HH}$ = 8.1)	5.52 (ddd)	2.15 ($^2J_{HH}$ = 17.4, $^3J_{HH}$ = 4.2, 1.6)	2.95 ($^2J_{HH}$ = 17.3, $^3J_{HH}$ = 11.7, 3.4)	c	0.42 (dddd)	5.59
143	Ph	H	H	Me	Me	c	c	7.28	5.76	5.34	2.38	3.88	c	1.52	5.64

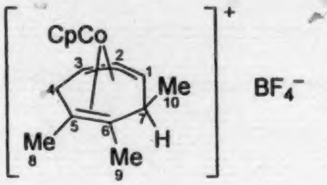
[a] In acetone-d_6. [b] Missing J values due to either overlapping or low-intensity signals. [c] Not applicable due to a non-hydrogen substituent. [d] J values from sample in $CDCl_3$.

Figure 4.1. Conformational comparison of Cp* and CpCo(η^5-cycloheptadienyl) complexes



The η^3,η^2- and η^5-cycloheptadienyl complexes (**132** and **133**) obtained from 1-methylpentadienyl complex **72** and 2-butyne are representative examples of the cationic η^3,η^2- and η^5-cycloheptadienyl complexes, respectively, and are discussed in detail since the spectra are simplified by the presence of multiple methyl groups.

Figure 4.2. [CpCo(η^3,η^2-1-*endo*,2,3-trimethylcycloheptadienyl)]$^+$[BF$_4$]$^-$ (**132**)



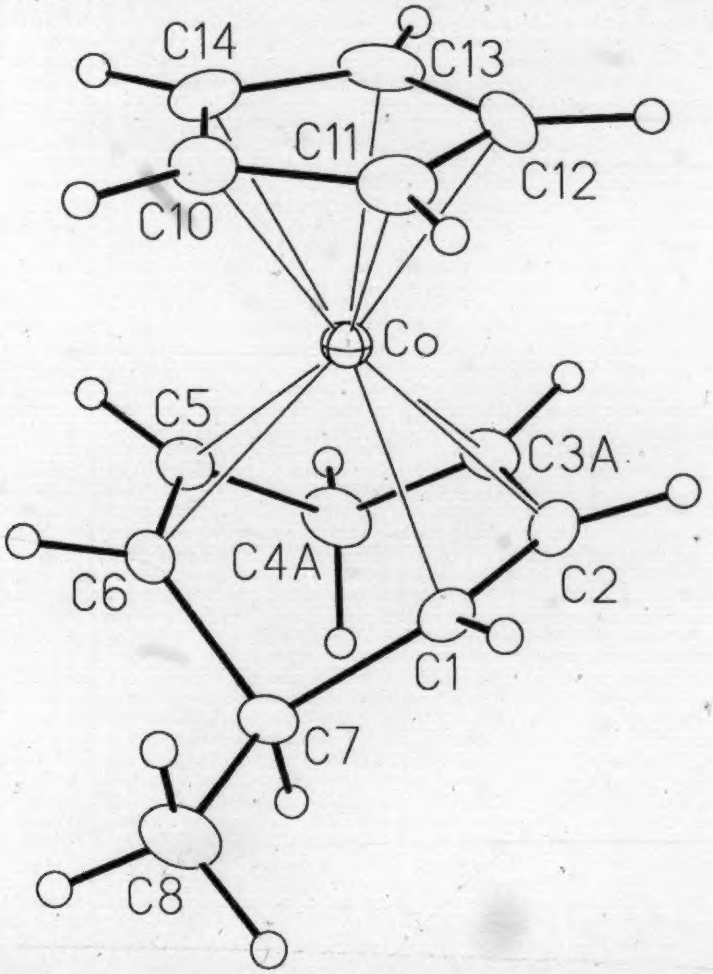
The elemental composition of complex **132** was determined by mass spectrometry and verified for the bulk material by elemental analysis. The IR spectrum reported $\nu_{C\text{-}H}$ (3113, 2972 cm^{-1}) and $\nu_{C=C}$ (1522, 1468, 1435, 1412 cm^{-1}) absorptions consistent with the presence of alkene moieties. The ^{1}H NMR spectrum includes ten chemical shifts, integrating to 20 protons. The most downfield chemical shift (δ 5.48, 5H) is a singlet assigned to the cyclopentadienyl ancillary ligand. The next chemical shift upfield (δ 5.32) is assigned to one of the terminal η^3-allyl protons (H_3). The chemical shift is slightly upfield from the chemical shift of the H_2/H_4 protons (δ 5.45-5.90) of the starting η^5-

pentadienyl complexes, indicating that H_3 is more shielded by the electron density on the terminal allyl. Due to poor resolution, the coupling constants for H_3 could not be measured. The next chemical shift upfield (δ 4.86) is assigned to the other terminal allyl (H_1) proton, shielded by the two nearby methyl substituents (H_8 and H_9). The H_1 proton couples to central proton H_2 ($^3J_{HH}$ = 6.7 Hz) and to the neighboring methylene protons (H_4, $^3J_{HH}$ = 4.5 Hz). The central allyl proton, H_2, is assigned to the next chemical shift upfield (δ 4.14), in part due to the characteristic triplet multiplicity and $^3J_{HH}$ coupling (*cis*, 7.3 Hz) to the neighboring terminal allyl protons (H_1 and H_3). The chemical shifts of the methylene protons (H_{4endo}, δ 3.12; H_{4exo}, δ 2.63; H_{7exo}, δ 2.70) reflect the chemical environment and proximity to the deshielding effects of the cobalt metal centre. The *endo* proton is approximately 0.4 ppm downfield in comparison with the *exo* protons. The two H_4 protons exhibit strong $^2J_{HH}$ geminal coupling (14.0-14.2 Hz) to each other and $^3J_{HH}$ vicinal coupling to H_3 (*endo*, 9.3 Hz; *exo*, 4.6 Hz). The proton assigned to H_{7exo} appears as a triplet since the $^3J_{HH}$ vicinal coupling to H_1 and H_{10} are approximately the same (6.2 Hz). Two of the methyl groups (H_8/H_9) are singlets assigned to the next upfield chemical shifts (δ 2.09 and δ 1.92, respectively). The chemical shift of these methyl protons is similar to those assigned to the internal and terminal methyl protons of the η^5-pentadienyl complexes (internal, δ 2.39; terminal, δ 1.68-1.75). The most upfield signal (δ 1.52, doublet) is assigned to the three methyl protons of H_{10}– the *endo*-methyl group on C_7 – and possesses the typical stereochemistry of the 1-substituent in [5+2] cycloaddition reactions with 1-substituted pentadienyl complexes. The H_{10} protons exhibit $^3J_{HH}$ coupling to H_{7exo} (7.0 Hz).

Two-dimensional ^{1}H NMR spectroscopy confirmed the structural assignments and coupling relationships determined from analysis of the one-dimensional ^{1}H NMR spectroscopic data. The chemical shift assigned to the two terminal allyl protons, H_1 and H_3 are coupled to the central H_2 proton. The chemical shift assigned to H_3 couples to H_{4endo} yet H_1 does not exhibit the expected coupling with H_{7exo}. Based on the X-ray crystal data for the related η^3,η^2-1-*endo*-methylcycloheptadienyl complex **130** (Figure **4.3**), and specifically a torsional angle for C_2-C_1-C_7-C_8 of 171.8[2]°, the absence of coupling between H_1 and H_{7exo} would be due to the Karplus curve and the near 90 deg. torsional angle of C_2-C_1-C_7-H_7. Therefore, GCOSY spectral data provide definitive identification of the assignments of H_1 and H_3. As well, from the GCOSY spectral data, the H_4 methylene protons exhibit strong $^{2}J_{HH}$ geminal coupling to each other, while the H_{7exo} proton displays strong $^{3}J_{HH}$ vicinal coupling to the protons of H_{10}.

The ^{13}C NMR spectrum consists of nine observed signals, due to the symmetry in the Cp ligand as well as the vanishingly low intensity of quaternary carbons (C_5 and C_6 were missing). Three signals are clustered around δ 88, which could be assigned to the Cp ligand, C_2 and C_3. The terminal allyl carbon (C_1) is assigned to the signal at 48.96 ppm, due to conformational distortion induced by the nearby methyl group. The two signals at δ 32.05 and δ 31.39 are assigned to either of the methylene or methine carbons; the methyl group carbons (C_8, C_9 and C_{10}) are assigned to the signals δ 23.70, δ 17.98 and δ 16.00.

Figure 4.3. ORTEP for Complex **130** from University of Alberta Department of Chemistry Structure Determination Laboratory Report # JMS0585



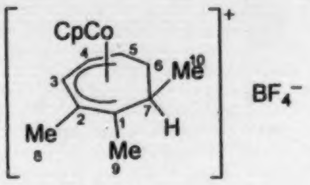
Final Residuals: $R_1 = 0.0336$; $wR_2 = 0.0870$. Data obtained at -80 °C. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

Selected Bond Distances (Å): Co-C1, 2.112(2); Co-C2, 2.055(2); Co-C3A, 2.089(5); Co-C4B, 2.146(9); Co-C5, 2.074(2); Co-C6, 2.115(2); C1-C2, 1.385(4); C1-C7, 1.511(3); C2-C3A, 1.368(6);C2-C3B, 1.556(9); C3A-C4A, 1.490(8); C4A-C5, 1.527(7); C3B-C4B, 1.501(12); C4B-C5, 1.323(10); C5-C6, 1.381(4); C6-C7, 1.506(3); C7-C8, 1.515(4)

Selected Bond Angles (deg.): C1-C2-C3A, 125.7(3); C1-C2-C3B, 117.7(4); C2-C3A-C4A, 123.5(5); C3A-C4A-C5, 102.2(4); C2-C3B-C4B, 101.9(6); C2-C3A-C4A, 123.5(5); C3A-C4A-C5, 102.2(4); C2-C3B-C4B, 101.9(6); C3B-C4B-C5, 126.8(7); C4A-C5-C6, 119.6(3); C4B-C5-C6, 126.4(4); C5-C6-C7, 123.3(2); C2-C1-C7, 124.4(2); C6-C7-C8, 112.3(2); C5-C6-C7-C8, 120.0(2); C2-C1-C7-C8, 171.8(2).

More specific assignments required the use of correlated ^{1}H-^{13}C spectroscopy. The gHSQC spectrum provided sufficient detail for the definitive assignments of all but one of the non-quaternary carbons. The assignment of the Cp ligand to δ 88.96 was confirmed by the correlated spectrum. The carbon assigned to δ 88.85 was identified as C_2, and the other carbon in the region was assigned by default as C_3. The assignment of C_1 was confirmed by the gHSQC spectral data, while C_7 was identified as δ 32.05 and C_4, δ 31.39. The assignment of the methyl groups was unambiguous and somewhat unexpected: δ 23.70, C_8; δ 17.98, C_{10}; and δ 16.00, C_9. The slight differences in chemical shifts are due to the differences in conformation and the shielding effects of the nearby metal centre and, perhaps, the Cp ring anisotropy.

Figure 4.4. [CpCo(η^5-1-*endo*,2,3-trimethylcycloheptadienyl)]$^+$[BF$_4$]$^-$ **(133)**



Mass spectroscopy confirms the elemental composition of the η^5-isomer, yet provides no support for the claim of isomerization. The NMR spectral data for complex **133** clearly indicate the formation of a new compound and suggest the assignment of a fully-conjugated η^5-isomer by comparison to many previously characterized and assigned complexes in the Cp* series. The most downfield signal (δ 7.21) is assigned to the central proton of the η^5-pentadienyl fragment. The chemical shift is within the range of the typical chemical shift of the central proton of an η^5-pentadienyl ligand (δ 7.00-7.38). The next chemical shift upfield (δ 5.59), a 5H singlet, is assigned to the protons of the Cp ligand. The Cp singlet overlaps with the next upfield chemical shift, at 5.52 ppm. This signal was initially assigned to the H_4 proton, since the chemical shift was similar to that of H_2/H_4 protons of the η^5-pentadienyl ligand (δ 5.45-5.90). The multiplicity (t) of the next signal upfield as well as the chemical shift itself suggested, however, that H_5 is more likely responsible for the signal at 5.52 ppm and H_4 appears instead at 5.21 ppm. The H_4 proton therefore, exhibits $^3J_{HH}$ vicinal coupling of similar magnitude to H_3 and H_5 (thus, a triplet), while H_5 exhibits $^3J_{HH}$ vicinal coupling to three protons with differing magnitudes. The two H_6 protons are assigned to the signals at δ 2.95 and δ 2.15. Both exhibit mutual $^2J_{HH}$ geminal coupling (17.4 Hz). The H_{6endo} proton also exhibits $^3J_{HH}$ vicinal coupling to the H_5 proton (3.4 Hz) as well as H_{7exo} (11.7 Hz); the H_{6exo} proton exhibits $^3J_{HH}$ vicinal coupling to the H_5 proton (3.4 Hz) as well as H_{7exo} (4.2 Hz);. The most downfield methyl group (2.50 ppm, singlet) is assigned to H_8; the other methyl singlet (1.75 ppm) is assigned to H_9, based on the relative chemical shifts of methyl groups in the open η^5-pentadienyl complexes. Interestingly, the two methyl groups are slightly upfield in comparison with those in the η^3,η^2-isomer due to greater shielding from the metal centre (based on a more planar configuration for the η^5-cycloheptadienyl ring). The third methyl group (H_{10}) is unambiguously assigned to the chemical shift at 0.97 ppm, since it is the only methyl (3H) doublet in the molecule. The methyl doublet displays $^3J_{HH}$ coupling (6.8 Hz) to H_{7exo}. The most upfield signal is assigned to the *exo* proton of C_7. The H_{7exo} proton exhibits $^3J_{HH}$ coupling to H_{10} (6.9 Hz) and the methylene protons of C_6 (*endo*, 11.7 Hz; *exo*, 4.6 Hz).

Structural assignments were also confirmed by two dimensional NMR spectroscopy (^{1}H GCOSY). The most downfield signal (H_3) displays strong $^3J_{HH}$ coupling to H_4 and long-range coupling to H_8 and H_9, but weak coupling to H_5. The next signal (H_5, δ 5.52) exhibits strong $^3J_{HH}$ coupling to H_4 , H_{6exo} and H_{6endo}. The signal at 5.21 ppm displays long-range $^4J_{HH}$ coupling to H_{6endo}. Therefore, the staggered structural assignment (H_3, δ 7.21; H_4, δ 5.21; H_5, δ 5.52), though unexpected, is certainly correct. The H_6 methylene protons display $^2J_{HH}$ geminal coupling to each other and $^3J_{HH}$ to H_{7exo}. The final coupling data from the GCOSY spectrum reflect the $^3J_{HH}$ vicinal coupling of the methyl doublet (H_{10}) and H_{7exo}.

The ^{13}C NMR spectral data contained eleven signals, reflecting the symmetry in the Cp ancillary ligand and dissymmetry in the cycloheptadienyl ligand. The six most downfield signals are in the alkenyl region and correspond to C_1-C_5 and the Cp carbons. The strongest signal (89.39 ppm) is typical of the Cp ancillary ligand. The near two signals upfield correspond to the methylene and methine carbons. One would expect the carbon with the greater substitution (H_7) to correspond to the more downfield signal (δ 50.56). The three most upfield carbon signals are assigned to the methyl carbons. The most upfield carbon is assigned C_{10}, due to shielding from the metal centre; the other two are difficult to distinguish without further data.

The ^{1}H-^{13}C gHSQC spectrum allowed the unambiguous assignment of all non-quaternary carbons (C_3-C_{10} and Cp). The most interesting correlation is between the two alkyl methylene/methine carbons and their respective protons. The more downfield carbon (δ 50.56) correlates to the two H_6 protons, while the more upfield carbon (δ 37.00) correlates to H_{7exo}. This spectral data support Dzwiniel's determination of the conformational distortion/staggering of C_6 and C_7. Even though C_7 is more substituted, the carbon nucleus is more shielded due to its proximity to the metal centre. Correlated spectral data also support the unusual assignment of H_4 and H_5, since the carbon data is consistent with the trend found in the ^{13}C NMR data of open η^5-pentadienyl complexes ($C_3 > C_2/C_4 > C_1/C_5$). As well, the assignment of C_9 to the more downfield (δ 23.53) signal is consistent with the high degree of branching, due to nearby C_8 and C_{10}.

The gHMBC spectral data confirm the previous structural assignments derived from $^3J_{CH}$ coupling (some $^2J_{CH}$ coupling is observed as well) and provide a means of identifying the quaternary carbons. The most characteristic correlation for C_1 and C_2 is the correlation between δ 110.52 and H_{10}. It is possible that the correlation is an example of $^4J_{CH}$ coupling; however, it is more reasonable to assume that δ 110.52 is correlated to C_1.

Most of the other cycloheptadienyl complexes reflect the same level or greater of spectroscopic complexity, due to additional protons (and the consequent coupling) or mixtures of η^3,η^2- and η^5-isomers. The cycloheptadienyl complexes from the [5+2] cycloaddition reactions of the unsubstituted complex **71** (and the one from the symmetrical 1,5-dimethylpentadienyl complex **78**) are simplified by the higher symmetry of the cycloheptadienyl ligand.

C. Correlation of pentadienyl structure and cyclization reactivity

As mentioned in the Chapter Two, the X-ray crystal structures of the various open pentadienyl complexes exhibited interesting variation in bond lengths. Since the 1-substituted pentadienyl complexes have a much higher reactivity towards alkynes than any other substitution pattern, it was thought that a careful analysis of the X-ray crystal data, and specifically the C-C and C-Co bond lengths, might shed light on this relationship between structure and reactivity toward cycloaddition.[114]

As proposed above (Scheme **4.9**), the Co(III)-mediated [5+2] cycloaddition reaction is thought to proceed through an η^3-pentadienyl intermediate, which dissociates the pendant vinyl in order to open a coordination site for an alkyne unit. The 1- and 2-substituted pentadienyl ligands have two options through which to proceed – dissociation of the terminally-substituted vinyl or the terminally-unsubstituted vinyl. It is postulated that the more substituted end of the pentadienyl is more willing to dissociate due to weaker back-bonding of the more substituted (electron-rich) alkene fragment. This hypothesis, upon first glance, is supported by some of the X-ray crystal data from Cp and Cp* pentadienyl complexes (Cp, Figure **2.6**, Tables **2.5**-**2.7**.; Cp*, Figure **4.5**, Tables **4.4**-**4.6**).

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[114] Ylijoki, K. E. O.; Witherell, R. D.; Kirk, A.; McDonald, R.; Ferguson, M. J.; Stryker, J. M. "Co-Mediated [5+2] Cycloaddition Reaction: Structure/Reactivity Relationship of η^5-Pentadienyl Complexes." Poster, CSC, Winnepeg, 2007.

Figure 4.5. C-C bond lengths of pentadienyl ligands of Cp*Co-pentadienyl complexes

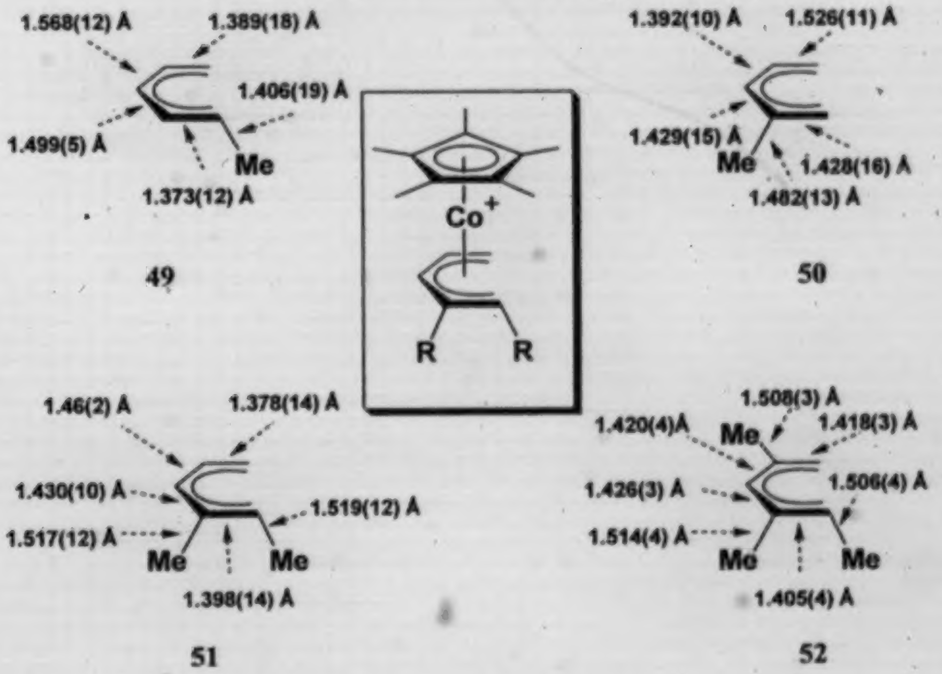
1.568(12) Å
1.389(18) Å
1.406(19) Å
1.499(5) Å
Me
1.373(12) Å
49
Co$^+$
R
R
1.392(10) Å
1.526(11) Å
1.429(15) Å
Me
1.428(16) Å
1.482(13) Å
50
1.46(2) Å
1.378(14) Å
1.430(10) Å
1.519(12) Å
1.517(12) Å
Me
Me
1.398(14) Å
51
1.508(3) Å
1.420(4)Å
Me
1.418(3) Å
1.426(3) Å
1.506(4) Å
1.514(4) Å
Me
Me
1.405(4) Å
52

Table 4.4. Co-C bond lengths (Å) of pentadienyl ligands of [Cp*Co(η^5-pentadienyl)]$^+$PF$_6^-$ complexes[a]

Atom1-Atom2	*1-Me*	*2-Me (A)*	*2-Me (B)*	*1,2-diMe*	*1,2,4-triMe*
Co-C1	2.176(3)	2.189(11)	2.102(14)	2.195(7)	2.181(2)
Co-C2	2.018(5)	2.058(13)	1.949(12)	2.086(7)	2.090(2)
Co-C3	2.082(11)	2.005(5)	1.941(6)	2.007(6)	2.060(3)
Co-C4	2.037(3)	2.043(8)	2.025(8)	2.00(2)	2.067(2)
Co-C5	2.054(9)	2.212(8)	2.208(7)	2.147(19)	2.086(3)

Table 4.5. C-C bond lengths (Å) of pentadienyl ligands of [Cp*Co(η^5-pentadienyl)]$^+$PF$_6^-$ complexes[a]

Atom1-Atom2	*1-Me*	*2-Me (A)*	*2-Me (B)*	*1,2-diMe*	*1,2,4-triMe*
C1-C2	1.373(12)	1.428(16)	1.42(2)	1.398(14)	1.405(4)
C2-C3	1.499(5)	1.429(15)	1.380(18)	1.430(10)	1.426(3)
C3-C4	1.568(12)	1.392(10)	1.313(11)	1.46(2)	1.420(4)
C4-C5	1.389(18)	1.526(11)	1.537(11)	1.378(14)	1.418(3)
C1/2-C6	1.406(19)	1.482(13)	1.536(12)	1.519(12) – C1-C6	1.506(4) – C1-C6
C2-C7				1.517(12)	1.514(4)
C4-C8					1.508(3)

Regardless of the relationship of structure to reactivity, the solid state structure for many of these pentadienyl ligands is distorted from the expected planar, fully delocalized, η^5-pentadienyl ligand. In fact, Cp*Co(pentadienyl) complex **49** appears to be closer to an η^3,η^2-coordinated unit, with the 1-methyl substituent on the η^2-olefin moiety, than an η^5-isomer. Cp*Co(1-methylpentadienyl) complex **50**, on the other hand, appears to be η^4,η^1-coordinated. In addition, both Cp* examples have an internal standard for the expected sp^2-sp^3 (single) bond distance – the bond from the pentadienyl carbon (C_1 or C_2) to the methyl group (C_6). In complex **49**, the distance between C_2-C_3 is longer than C_1-C_6, the known single bond. As well, in complex **50**, the known single bond, C_1-C_6, is shorter than C_4-C_5. One would expect, therefore, that complex **49** would be more reactive toward cycloaddition reactions, due to the higher lability of the substituted vinyl, whereas complex **50** should be less reactive, due to the decreased lability of the pendant 2-methallyl unit, which is consistent with observations.

In the case of the pentadienyl ligands in the Cp complexes, on the other hand, no such structural X-ray trend exist. 1-Methylpentadienyl complex **72**, which is very reactive towards cycloaddition reactions, has an undistorted structure similar to complex **50**. As well, the bond distances determined for 1-trimethylsilylpentadienyl complex **74** seem to reflect a η^2,η^2,η^1-bonding pattern, yet the reactivity of this complex is similar to that of complex **72**.

Therefore, the X-ray structures appear to reflect solid-state distortions not directly related to the reactivity observed in the cycloaddition reaction. As more reactivity studies, as well as crystal structures, are gathered on these η^5-pentadienyl- and both η^3,η^2- and η^5-cycloheptadienyl complexes, it should become more clear exactly how the substitution pattern of the pentadienyl ligand influences the reactivity of the complex in [5+2] cycloaddition reactions.

III. Conclusion

A modest range of alkyl-substituted CpCo(cycloheptadienyl) complexes have been prepared in moderate to excellent yields via thermal [5+2] cycloaddition reactions between CpCo(η^5-pentadienyl) complexes and various alkynes. Some of the reaction yields are lower than those observed in the Cp* system, yet the Cp ligand system uniquely allows, in many cases, the isolation of the interrupted η^3,η^2-cycloheptadienyl complex from cycloaddition reactions with acetylene and 2-butyne. The thermal isomerization of η^3,η^2- to η^5-hapticity was demonstrated for 1,2,3-trimethylcycloheptadienyl complex **132** and is likely generalizable to all such η^3,η^2-compounds, as suggested by the presence of the fully-conjugated compounds in reaction mixtures for cases involving the more reactive pentadienyl complexes (e.g., complex **73**) or the use of elevated temperatures.

The [5+2] cycloaddition reactions proceed for unsubstituted and 1-substituted pentadienyl complexes, but do not undergo clean conversion in the case of 2-substituted or any disubstituted pentadienyl complexes. The Cp ancillary ligand thus slightly expands the reaction scope in comparison with Cp*, yet does not resolve all of the limitations experienced with Cp*.

In addition, the regioselectivity of the [5+2] cycloaddition reactions with unsymmetrical alkynes is similar to that observed for the Cp* system. It is difficult to predict the steric influence that the ancillary ligand methyl groups impose on the formation of cycloheptadienyl complexes and unclear how the regioselectivity observed with the Cp ancillary ligand might differ from that of the Cp* system. In the reactions of electron-deficient alkynes, one also expects to see a difference between the two ligand systems, due to the differing electronic demands of the ancillary ligand; however, this too was not observed experimentally. The Cp and Cp* systems exhibit similar trends in regioselectivity, exhibiting differentiation only in cases of significant steric bias between the alkyne substituent and the pentadienyl substituent. These issues obviously require the development of an entirely new reaction system.

In general, the [3+2+2] and [5+2] cycloaddition reactions are complementary processes that provide access to different cycloheptadienyl complexes. The [5+2] cycloaddition reaction using CpCo provides access to a wider range of η^3,η^2-isomers than available from the Cp* system or, of course, from the [3+2+2] cycloaddition reaction, which delivers exclusively the η^5-isomer. The [3+2+2] cycloaddition reaction does provide access to cycloheptadienyl complexes with two substituents at C_7, which are inaccessible with [5+2] pentadienyl/alkyne cycloaddition reactions and would only become accessible if the [5+2] cycloaddition reaction could be extended to alkenes.

Chapter Five: Future Considerations

The reactivity and scope of the CpCo [5+2] pentadienyl/alkyne cycloaddition reaction offers limited but promising potential for the general synthesis of substituted seven-membered rings. A representative sample of the η^3,η^2- and η^5-cycloheptadienyl complexes, however, need to be evaluated for reactivity toward nucleophilic addition (with both hard and soft nucleophiles) and subsequent oxidative decomplexation to demonstrate the utility of the methodology for organic synthesis. The decomplexation will likely proceed with greater facility using CpCo than Cp*Co, since the Cp ancillary ligand is less electron-rich and, therefore, the (oxidized) cycloheptadiene ligand is presumably less tightly bound to the dicationic metal centre.

The scope of the reaction is limited by the modest yields and our inability to access a wider range of substituted η^5-pentadienyl complexes. With both methods of complexation (cf., Chapters Two and Three), the protic reaction conditions and the sensitivity of the organic substrate (and multiply-substituted 1,4-pentadien-3-ols in particular) hinders the formation of highly substituted η^5-pentadienyl complexes. Complexation of the 1,4-pentadien-3-ol substrate class is in competition with various decomposition pathways, most notably oligomerization and the formation of cyclopentadienes via protonation, dehydration and Nazarov cyclization. In particular, there is little evidence to show that the 1,4-diene exchanges with the ethylene ligands favourably to form an intermediate cobalt 1,4-diene complex (likely due to coordination strain/poor orbital overlap). All prior attempts to form and isolate such a cobalt η^4-1,4-

diene intermediate have been unsuccessful, yielding primarily decomposition products.[115]

The 2,4-pentadien-1-ol substrate class (e.g., **37**, Schemes **2.4** and **3.9**), however, will likely address the issues of *in situ* decomposition of the organic substrate and provide a ready means to access more substituted η^5-pentadienyl complexes. Conjugated dienes are well-established to participate in ligand exchange with both starting complexes **34** and **35** and form isolable cobalt diene complexes.[64] Therefore, with 2,4-pentadien-1-ols, one could presumably complex the substrate, isolate the diene intermediate if desired, and then dehydrate the alcohol by protonation to form the η^5-pentadienyl complex after stereochemical isomerization. The organic substrate would be coordinated prior to the addition of an acid, and therefore, would not be subjected to the harsh acidic conditions thought responsible for much of the decomposition of 1,4-pentadien-3-ols.

Since the Cp ancillary ligand provides certain advantages of scope over the Cp* ligand system, yet provides no improvement in regioselectivity, it appears reasonable to evaluate an unsymmetrical cyclopentadienyl ligand, such as *t*-BuCp or even Me_4C_5H. In addition, concurrently, an ancillary ligand system with a significant steric bias, such as Tp* or an anionic tripodal borane ligand,[116] should be evaluated, to find a ligand that balances greater regioselectivity against possible limitations in reactivity.

These modifications and explorations will hopefully provide the necessary direction for developing the cobalt-mediated [5+2] cycloaddition reaction, providing greater access to an even wider array of substituted cycloheptadienyl complexes and, ultimately, functionalized and substituted cycloheptadienes appropriate for use in organic synthesis.

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[115] Witherell, R. D., Unpublished results.

[116] Dodds, C. A.; Lehmann, M.-A.; Ojo, J. F.; Reglinski, J.; Spicer, M. D. *Inorg. Chem.* **2004**, *43*, 4927.

Experimental Procedures

Reagents and Methods. All manipulations on air-sensitive compounds were performed under an argon or nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere glove box equipped with an internal freezer maintained at -35 °C. Vacuum transfer of volatile reagents was performed at high vacuum (10^{-5} mm Hg) using a MKS Baratron digital pressure transducer for measurement of gas pressure in known volume flasks. Hexane and pentane were distilled from potassium/benzophenone ketyl. Toluene, benzene, tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl. Reagent grade acetone was dried over boric oxide, degassed *via* three freeze-pump-thaw cycles, vacuum transferred and stored under nitrogen. Dichloromethane and acetonitrile were distilled over calcium hydride. Both ethyl acetate and nitromethane were dried over CaH_2 and then distilled. Crotonaldehyde was purified by fractional distillation (b. p. 104-105 °C). *N*-Trimethylamine *N*-oxide was dehydrated by sublimation (40 °C / 0.01 torr). Ethyne and ethene were used without further purification. Photolysis reactions were irradiated with a 450 Watt Hanovia mercury-vapor lamp placed six inches from the reaction vessel, all in an enclosed photolysis chamber.

IR spectra were recorded on a Nic-Plan FTIR microscope. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity-Inova 300 (^{1}H, 300 MHz), Varian Unity-Inova 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Varian Mercury 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), Varian Inova 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz), Varian DirectDrive 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) or a Varian Unity-Inova 600 (^{1}H, 600 MHz) spectrometer. High resolution mass spectra were obtained on an Applied Biosystems Mariner Biospectrometry Workstation (electrospray ionization) and elemental analyses were performed by the University of Alberta Microanalysis Laboratories.

Further Notes on Spectroscopic Methods. Chemical shifts are reported relative to residual protiated solvent. For ^{1}H NMR spectral data, values of the coupling constants are obtained directly from the spectrum. Although generally measured to ±0.1 Hz, *J* values are self-consistent only to ± 0.5 Hz. GCOSY denotes the standard COSY experiment, acquired using field gradients. Data for the ^{1}H-^{1}H COSY or GCOSY is presented such that correlations are listed only once. gHSQC experiments are recorded at the ^{13}C frequency of the spectrometer, while gHMQC and gHMBC are recorded at the ^{1}H frequency.

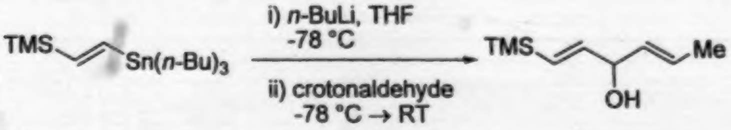
Atom labels for numbering system of cycloheptadienyl complexes. In order to avoid confusion in the discussion of the ^{1}H NMR spectral data, the numbering scheme employed by T. L. Dzwiniel for the Cp ligand system was applied herein.[2] The most upfield signal in the CpCo(η^5-cycloheptadienyl) complexes was assigned to the H_{7exo} atom and the neighboring methylene protons, H_6. In the case of η^3,η^2-cycloheptadienyl complexes, the assignment of C_7 was maintained, the other methylene is labeled C4 and the remaining atoms accordingly. In cases of 1-substituted η^5-pentadienyl complexes, the substituent is on the C_7 atom in both η^3,η^2- and η^5-complexes. When the cycloheptadienyl ligand has a mirror plane, the numbering system is maintained and both positions are reported.

The following compounds were prepared by published procedures: 1,4-hexadien-3-ol (**55**),[39,40,41] 1-phenyl-1,4-pentadien-3-ol (**56**),[42] 1-trimethylsilyl-1,4-pentadien-3-ol (**57**),[43,44] 5-methyl-1,4-hexadien-3-ol (**58**),[41,42,45,46] 4-methyl-1,4-hexadien-3-ol (**59**), 2-methyl-1,4-hexadien-3-ol (**60**),[39] 2,5-heptadien-4-ol (**61**),[41] 2-methyl-1,4-pentadien-3-ol (**62**),[41] 3-methyl-1,4-pentadien-3-ol (**63**),[48] 1-cyclopentene-1-methanol-α-ethenyl (**64**),[57] 1-cyclohexene-1-methanol-α-ethenyl (**65**),[50,51,52] 2-furan-1-methanol-α-ethenyl (**66**),[53] 3-furan-1-methanol-α-ethenyl (**67**),[54] and 2-dihydropyran-1-methanol-α-ethenyl (**68**).[55] All prepared pentadienols were distilled before use. The unsubstituted 1,4-pentadien-3-ol (**54**) was commercially available, and used without further purification.

The following materials were provided by generous researchers as indicated in parentheses: 4-methyl-1,4-hexadien-3-ol (**59**) (Witherell), 3,4,5-trimethyl-2,5-heptadien-4-ol (**69**) (Gauthier), 1-cyclopentenyl-magnesium bromide (Ylijoki), TMS-acetylene (Tykwinski group), and TIPS-acetylene (Tykwinski group). X-ray crystal data for Cp*Co(η^5-pentadienyl) complexes was provided by R. D. Witherell (JMS0423, JMS0452, JMS0520 and JMS0570).

Cobaltocene (**36**) was made by the addition of solid anhydrous $CoCl_2$ to a solution of lithium and cyclopentadiene in THF.[27] $CpCo(C_2H_4)_2$ (**34**) was prepared by the reduction of (**36**) with potassium in THF in the presence of excess (1 atm) ethylene.[26] $CpCo(CO)_2$ (**35**) was prepared by refluxing the cyclopentadiene in THF with $Co_2(CO)_8$.[64,66,67,68] Complexes (**36**) and (**34**) were purified by recrystallization in pentane.[26,28] Complex (**35**) was purified by low temperature recrystallization (f. p. 26.7 °C). CpCo(cyclopentadienyl)- and CpCo(cycloheptadienyl) complexes were purified by recrystallization by dissolving the sample in dichloromethane in a small tube, capped with an NMR tube cap with a pin-hole and immersed in a solution of diethyl ether (pin-hole diffusion). One CpCo(η^3-pentadienyl)carbonyl complex **(99)** was also purified using recrystallization by pin-hole diffusion (nitromethane/diethyl ether).

Chapter Two Experimental Section



70

1-Trimethylsilyl-1,4-hexadien-3-ol (70). A three-neck flask, reflux condenser, addition funnel, and vacuum inlet were dried and assembled. The flask was charged with 1-tributylstannyl-2-trimethylsilyl-ethylene (10.0 g, 25.73 mmol)[117] and THF (62 mL) under Ar and cooled to -78 °C. The addition funnel was charged with *n*-BuLi (2.5 M in hexanes) (11.3 mL, 28 mmol), which was added dropwise to the reaction flask and allowed to stir for 30 minutes. The reaction mixture turned yellow. The addition funnel was removed under positive Ar pressure and crotonaldehyde (2.0 g, 2.4 mL, 35.7 mmol) in THF (5 mL) was added dropwise via syringe. The reaction mixture was warmed to RT and allowed to stir for an additional 15 minutes. Then the reaction mixture was diluted with diethyl ether (100 mL), washed with saturate aqueous ammonium solution (50 mL), water (50 mL), and brine (50 mL), dried (sodium sulphate), and the solvent removed in vacuo. The oil was purified by flash column chromatography on silica gel using hexane-diethyl ether (10:1) mixture as eluent. Compound **70** exists as an isomeric mixture, 76:24 (*E*/*Z* at 1-TMS). **1-*E*-TMS isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (dd, *J* = 5.0 Hz, *J* = 18.8 Hz, 1H, H_2), 5.88 (dd, *J* = 1.4 Hz, *J* = 18.7 Hz, 1H, H_1), 5.72 (ddd, *J* = 1.1 Hz, *J* = 6.5 Hz, *J* = 15.3 Hz, 1H, H_5), 5.50 (ddd, *J* = 1.6 Hz, *J* = 6.8 Hz, *J* = 15.3 Hz, 1H, H_4), 4.55 (dq, *J* = 5.0 Hz, 1H, H_3), 1.72 (ddd, *J* = 0.8 Hz, *J* = 1.6 Hz, *J* = 6.5 Hz, 3H, H_6), 0.08 (s, 9H, H_7); GCOSY (400 MHz, $CDCl_3$) δ 6.05 (H_2) ↔ 5.88 (H_1), 4.55 (H_3); 5.88 (H_1) ↔ 4.55 (H_3); 5.70 (H_5) ↔ 5.50 (H_4), 4.55 (H_3), 1.72 (H_6); 5.55 (H_4) ↔ 4.55 (H_3), 1.72 (H_6); 4.55 (H_3) ↔ 1.60 (O$\underline{H}$). **1-*Z*-TMS isomer**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (overlapping with *E*-H_2, 1H, m, H_2), 5.86 (overlapping with *E*-H_1, *1H*, m, H_1), 5.65 (overlapping with *E*-H_5, 1H, ddd, *J* = 0.9 Hz, *J* = 6.4 Hz, *J* = 13.5 Hz, H_5), 5.48 (overlapping with *E*-H_4, 1H, m, H_4), 4.05 (1H, dq, H_3), 1.70 (overlapping with *E*-H_6, 3H, ddd, *J* = 0.7 Hz, *J* = 1.5 Hz, *J* = 6.4 Hz, H_6), 0.08 (9H, s, TMS Me, H_9); GCOSY (400 MHz, $CDCl_3$) δ 6.03 (H_2) ↔ 5.86 (H_1); 5.65 (H_5) ↔ 5.48 (H_4), 1.70 (H_6); 5.48 (H_4) ↔ 4.05 (H_3), 1.70 (H_6). **Isomeric mixture**: IR (microscope, cm^{-1}): 2956 (s), 2926 (s), 2872 (s), 1724 (m), 1464 (m), 1248 (m), 864 (s), 839 (s). HRMS *m/z* calculated for $C_{12}H_{25}OSn$ (M^+): 305.09274; found: 305.09256.

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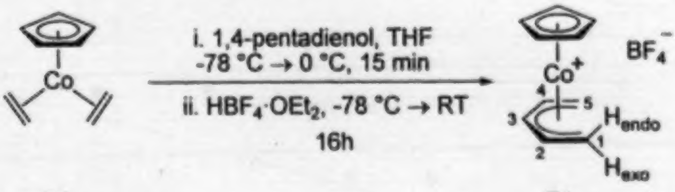
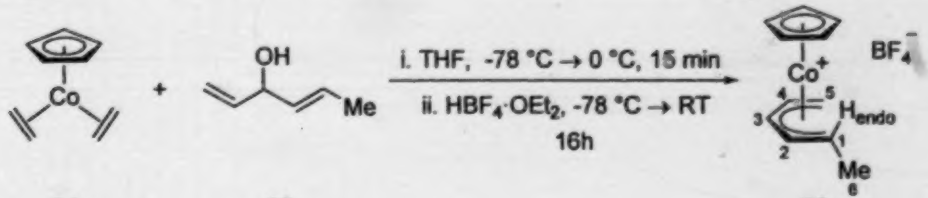
[117] *Trans*-1-tributylstannyl-2-trimethylsilyl-ethene ($Bu_3SnCHCHSiMe_3$) was previously synthesized for the literature preparation of compound **57** (1-TMS-1,4-pentadien-3-ol).[44]



34 **71**

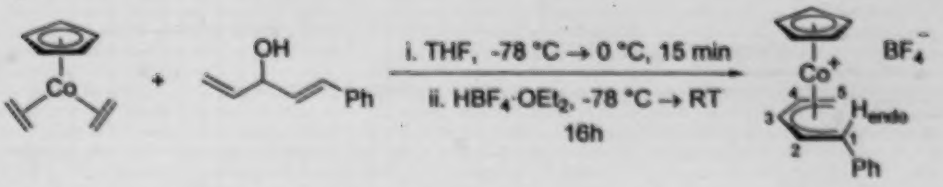
[CpCo(η^5-pentadienyl)]$^+$BF$_4^-$ (71). In the drybox, complex **34** (0.030 g, 0.1705 mmol) was weighed into a Schlenk flask and dissolved in tetrahydrofuran (3 mL). As well, excess tetrafluoroboric etherate solution (54% solution of acid in diethyl ether) was added to a small vial and capped with a septum. The Schlenk flask and capped vial were taken outside the box and the flask was cooled to -78 °C while under an Argon atmosphere. After 5 to 10 minutes at -78 °C, the pentadienol (15.8 mg, 18.2 μL, 0.1875 mol), itself at room temperature, was added via microsyringe into the stirring Schlenk flask. The flask was warmed to 0 °C and allowed to stir for 10 minutes (bubbling occurred). After stirring, the flask was again cooled to -78 °C, and the acid (30.5 mg, 25.8 μL, 0.1875 mmol) was added via microsyringe (with positive Ar pressure). The reaction mixture was allowed to warm to room temperature overnight. In the morning, the flask was removed from the bath, the volatiles were removed *in vacuo*. The crude product was then purified using flash chromatography (silica gel, 3% methanol/dichloromethane). A light orange powder (36.9 mg, 78%) was obtained. Crystals suitable for an X-ray diffraction analysis were grown from pin-hole diffusion (dichloromethane/diethyl ether) at room temperature. For full data on this crystal structure, request report # JMS0603 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}): 3211 (s), 3078 (w), 1520 (w), 1455 (s), 1431 (s), 1412 (s), 1286 (w), 1080 (br), 921 (s), 852 (s). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.28 (tq, J = 1.0 Hz, J = 6.9 Hz, 1H, H_3), 5.95 (s, 5H, Cp), 5.90 (overlapping with Cp, dddd, J = 0.9 Hz, J = 6.8 Hz, J = 9.4 Hz, J = 16.2 Hz, 2H, H_2/H_4), 4.28 (dd, J = 2.8 Hz, J = 9.5 Hz, 2H, H_{1exo}/H_{5exo}), 2.03 (overlapping with solvent peak, dd, J = 0.8 Hz, J = 3.1 Hz, 2H, H_{1endo}/H_{5endo}); GCOSY (400 MHz, acetone-d_6) δ 7.28 (H_3) ↔ 5.90 (H_2/H_4), 4.28 (H_{1exo}/H_{5exo}), 2.03 (H_{1endo}/H_{5endo}); 5.90 (H_2/H_4) ↔ 4.28 (H_{1exo}/H_{5exo}), 2.03 (H_{1endo}/H_{5endo}); 4.28 (H_{1exo}/H_{5exo}) ↔ 2.03 (H_{1endo}/H_{5endo}); ^{13}C APT (100 MHz, acetone-d_6) δ 101.52 (-, C_3), 97.09 (-, C_2/C_4), 88.30 (-, Cp), 61.68 (+, C_1/C_5); ^1H-^{13}C gHMQC (400 MHz, acetone-d_6) δ 101.52 (C_3) ↔ 7.28 (H_3), 97.09 (C_2/C_4) ↔ 5.90 (H_2/H_4), 88.30 (Cp) ↔ 5.95 (Cp), 61.68 (C_1/C_5) ↔ 2.03, 4.28 (H_1/H_5); ^1H-^{13}C gHMBC (400 MHz, acetone-d_6) δ 101.52 (C_3) ↔ 4.28 (H_{1exo}/H_{5exo}), 2.03 (H_{1endo}/H_{5endo}), 97.09 (C_2/C_4) ↔ 4.28 (H_{1exo}/H_{5exo}); 61.68 (C_1/C_5) ↔ 7.28 (H_3). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (dt, *J* = 0.8 Hz, *J* = 6.8 Hz, 1H, H_3), 5.91 (dd, *J* = 2.8 Hz, *J* =6.9 Hz, 2H, H_2/H_4), 5.90 (s, 5H, Cp), 4.20 (ddd, *J* = 0.8 Hz, *J* = 2.4 Hz, *J* = 9.6 Hz, 2H, H_{1exo}/H_{5exo}), 1.70 (dd, *J* = 2.6 Hz, *J* = 11.7 Hz, 2H, H_{1endo}/H_{5endo}). Electrospray MS *m/z* calculated for $C_{10}H_{12}Co$ (M^+): 191.02655; found: 191.02665. Anal. calcd for $C_{10}H_{12}CoBF_4$: C, 43.21; H, 4.35; Found: C, 43.46; H, 4.34.



34 **55** **72**

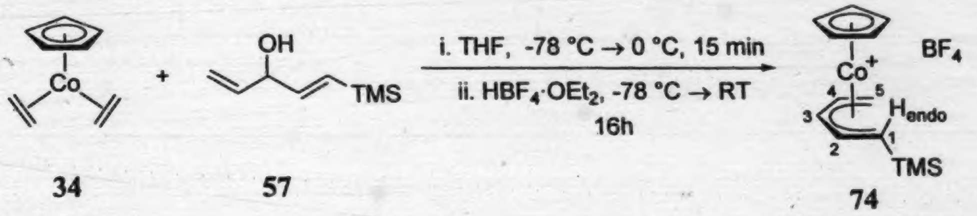
[CpCo(η^5-hexadienyl)]$^+$BF$_4^-$ (72). Complex **72** (red powder, 209 mg, 0.716 mmol, 87%) was prepared according to the detailed procedure given for complex **71** (starting bis[ethylene] **34**: 209.5 mg, 1.16 mmol; dienol **55**: 128 mg, 149 μL, 1.16 mmol; HBF_4, 180 μL, 1.16 mmol; ~10 mL THF). Crystals suitable for an X-ray diffraction analysis were grown from pin-hole diffusion (dichloromethane/diethyl ether) at room temperature. For full data on this crystal structure, request report # JMS0581 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}): 3120 (s), 3065 (s), 2981 (w), 2914 (w), 2859 (w), 1524 (m), 1452 (s), 1432 (s), 1381 (s); 1287 (s), 996.7 (br), 938 (s), 892 (s), 862 (s), 831 (s). ^1H NMR (400

MHz, acetone-d_6) δ 7.15 (dt, *J* = 0.8 Hz, *J* = 6.8 Hz, 1H, H_3), 5.80 (s, 5H, Cp), 5.72-5.81 (m, 2H, H_2+H_4), 4.21 (ddd, *J* = 0.8 Hz, *J* = 2.8 Hz, *J* = 9.2 Hz, 1H, H_{5exo}), 2.95 (ddd, $^4J_{1endo\text{-}3}$ = 0.8 Hz, $^3J_{1endo\text{-}6}$ = 6.4 Hz, $^3J_{1endo\text{-}4}$ = 12 Hz, 1H, H_{1endo}), 2.07 (overlapping with solvent peak, dd, *J* = 0.8 Hz, *J* = 3.2 Hz, 1H, H_{5endo}), 1.74 (dd, *J* = 0.8 Hz, *J* = 6.4 Hz, 3H, H_6); GCOSY (400 MHz, acetone-d_6): δ 7.15 (H_3) ↔ 5.75 (H_4), 5.73 (H_2), 4.21 (H_{5exo}), 2.07 (H_{5endo}); 5.75 (H_4) ↔ 4.21 (H_{5exo}), 2.07 (H_{5endo}); 5.73 (H_2) ↔ 2.95 (H_{1endo}), 1.74 (H_6); 4.21 (H_{5exo}) ↔ 2.07 (H_{5endo}); 2.95 (H_{1endo}) ↔ 1.74 (H_6); ^{13}C APT NMR (400 MHz, acetone-d_6): δ 97.17 (-, C_3), 96.58 (-, C_2 or C_4), 95.63 (-, C_2 or C_4), 88.52 (-, Cp), 85.42 (-, C_1), 59.99 (+, C_5), 22.57 (-, C_6); gHMQC (400 MHz, acetone-d_6): δ 97.17 (C_3) ↔ 7.15 (H_3); 96.58 (C_2 or C_4) ↔ (missing); 95.63 (C_2 or C_4) ↔ (missing); 88.52 (Cp) ↔ 5.80 (Cp); 85.42 (C_1) ↔ (missing); 59.99 (C_5) ↔ 4.21 (H_{5exo}), 2.07 (H_{5endo}); 22.57 (C_6) ↔ 1.74 (H_6); gHMBC (400 MHz, acetone-d_6): δ 96.58 or 95.63 (C_2 or C_4) ↔ 1.74 (H_6); 85.42 (C_1) ↔ 1.74 (H_6); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (t, *J* = 6.8 Hz, 1H, H_3), 5.65-5.75 (m, 2H, H_2+H_4), 5.62 (s, 5H, Cp), 4.14 (dd, *J* = 3.1 Hz, *J* = 9.3 Hz, 1H, H_{5xo}), 2.59 (dd, *J* = 6.4 Hz, *J* = 11.9 Hz, 1H, H_{1endo}), 1.73 (dd, *J* = 0.8 Hz, *J* = 3.2 Hz, 1H, H_{5xo}), 1.70 (d, *J* = 6.2 Hz, 3H, H_6). Electrospray MS *m/z* calculated for $C_{11}H_{14}Co$ (M^+): 205.04220; Found: 205.04227. Anal. calcd for $C_{11}H_{14}CoBF_4$: C, 45.25; H, 4.83; Found: C, 45.1697; H, 4.6506.



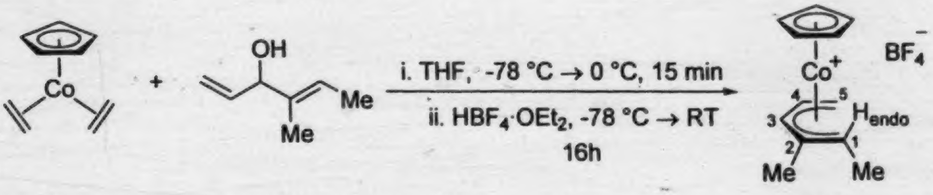
34 **56** **73**

[CpCo(η^5-1-phenylpentadienyl)]$^+$BF$_4^-$ (73). Complex **73** (dark red powder, 0.6587g, 1.86 mmol, 33%) was prepared according to the detailed procedure given for complex **71** (bis[ethylene] complex **34**: 1.01 g, 5.67 mmol; dienol **56**: 0.909 mg, 5.67 mmol; HBF_4, 0.869 mL, 5.67 mmol; ~25 mL THF). Even after several recrystallizations using pin-hole diffusion (dichloromethane/diethyl ether), the sample was not analytically pure. IR (microscope, cm^{-1}): 3120 (s), 1418 (s), 1284 (m), 1036 (br s), 1008 (s), 866 (s). ^{1}H NMR (400 MHz, acetone-d$_6$) δ 7.75 (dd, J = 2.1 Hz, J = 7.4 Hz, 2H, Ph), 7.46 (m, 3H, Ph), 7.38 (t, J = 7.3 Hz, 1H, H_3), 6.61 (dd, J = 7.3 Hz, J = 12.2 Hz, 1H, H_2), 5.88 (ddd, J = 6.8 Hz, J = 9.8 Hz, J = 12.0 Hz, 1H, H_4), 5.54 (s, 5H, Cp), 4.47 (dd, J = 2.8 Hz, J = 9.1 Hz, 1H, H_{5exo}), 3.85 (d, J = 12.0 Hz, 1H, H_{1endo}), 2.71 (dd, J = 3.2 Hz, J = 11.9 Hz, 1H, H_{5endo}); GCOSY (400 MHz, acetone-d$_6$) δ 7.75 (Ph) ↔ 7.46 (Ph); 7.38 (H_3) ↔ 6.61 (H_2), 5.88 (H_4); 6.61 (H_2) ↔ 3.85 (H_{1endo}); 5.88 (H_4) ↔ 4.47 (H_{5exo}), 2.71 (H_{5endo}); 4.47 (H_{5exo}) ↔ 2.71 (H_{5endo}); ^{13}C NMR (100 MHz, acetone-d$_6$): δ 130.32 (Ph), 130.27 (Ph), 129.96 (Ph), 128.22 (Ph), 96.20 (C_2-C_4), 91.04 (C_2-C_4), 89.33 (Cp), 85.75 (C_2-C_4), 50.20 (C_1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 2H, Ph), 7.50 (t, J = 7.4 Hz, 1H, H_3), 7.46 (m, 3H, Ph), 6.56 (dd, J = 12.3 Hz, J = 7.2 Hz, 1H, H_2), 5.86 (ddd, 1H, H_4), 5.41 (s, 5H, Cp), 4.30 (dd, J = 3.1 Hz, J = 9.3 Hz, 1H, H_{5exo}), 3.34 (d, J = 12.3 Hz, 1H, H_{1endo}), 2.12 (dd, J = 3.1 Hz, J = 12.1 Hz, H_{5endo}). gHMBC (400 MHz, acetone-d$_6$) attempted. Anal. calcd for $C_{16}H_{16}CoBF_4$: C, 54.28; H, 4.56; Found: C, 51.7282; H, 4.3812. Electrospray MS *m/z* calculated for $C_{16}H_{16}Co$ (M^+): 267.05785; Found: 267.05787.



[CpCo(η^5-1-trimethylsilylpentadienyl)]$^+$BF$_4^-$ (74). Complex **74** (dark red powder, 33.5 mg, 0.0958 mmol, 56%) was prepared according to the detailed procedure given for complex **71** (starting bis[ethylene] **34**: 30 mg, 0.171 mmol; dienol **57**: 34.4 μL, 0.188 mmol; HBF_4, 25.8 μL, 0.188 mmol; ~1 mL THF). Crystals suitable for an X-ray diffraction analysis were grown from pin-hole diffusion (dichloromethane/diethyl ether) at room temperature. For full data on this crystal structure, request report # JMS0704 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}): 3469 (br), 3125 (s), 3056 (m), 2942 (s), 2864 (s), 2804 (s), 2743 (w), 1725 (w), 1603 (w), 1492 (s), 1460 (s), 1412 (s), 1374 (s), 1251 (s), 1032 (br), 957 (s), 840 (s), 747 (w), 698 (w), 666 (w). ^1H NMR (400 MHz, acetone-d_6): δ 7.34 (t, J = 6.0 Hz, 1H, H_3); 6.05 (dd, J = 6.0 Hz, J = 14.8 Hz, 1H, H_2); 5.90 (overlapping with H_2, m [5H, s, Cp + m,1H, H_4], 6H, Cp+H_4); 4.30 (d, J = 7.2 Hz, 1H, H_{5exo}); 2.55 (dd, J = 1.9 Hz, J = 12.0 Hz, 1H, H_{5endo}); 1.73 (d, J = 14.8 Hz, 1H, H_{1endo}); 0.25 (s, 9H, H_6); GCOSY (400 MHz, acetone-d_6): δ 7.34 (H_3) ↔ 6.05 (H_2), 5.90 (H_4); 6.05 (H_2) ↔ 1.73 (H_{1endo}); 5.90 (H_4) ↔ 4.30 (H_{5exo}), 2.55 (H_{5endo}); 4.30 (H_{5exo}) ↔ 2.55 (H_{5endo}); ^{13}C APT (100.58 MHz, acetone-d_6): δ 102.30 (-, C_2); 98.91 (-, C_3); 97.52 (-, C_4); 87.46 (-, Cp);

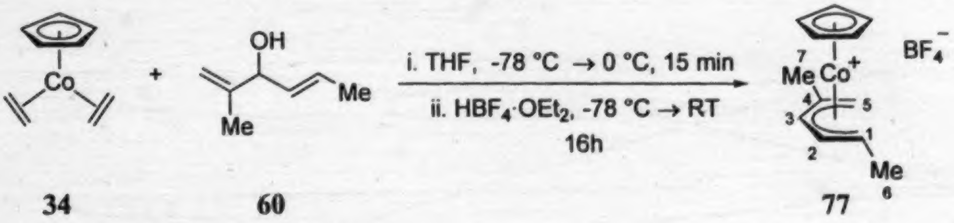
78.39 (-, C_1); 61.70 (+, C_5); -1.18 (-, C_6); gHMQC (600 MHz, acetone-d_6): δ 102.30 (C_2) ↔ 6.03 (H_2); 98.91 (C_3) ↔ 7.34 (H_3); 97.52 (C_4) ↔ 5.84 (H_4); 87.46 (Cp) ↔ 5.89 (Cp); 78.39 (C_1) ↔ 1.75 (H_{1endo}); 61.70 (C_5) ↔ 4.30 (H_{5exo}), 2.55 (H_{5endo}); -1.18 (C_6) ↔ 0.29 (H_6); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, J = 6.1 Hz, 1H, H_3); 5.92 (m, 2H, H_2+H_4); 5.75 (s, 5H, Cp); 4.25 (d, J = 7.0 Hz, 1H, H_{5exo}); 2.12 (d, J = 7.1 Hz, 1H, H_{5endo}); 1.21 (m, 1H, H_{1endo}); 0.30 (s, 9H, H_6); GCOSY (400 MHz, $CDCl_3$): 7.42 (H_3) ↔ 5.92 (H_2+H_4); 5.92 (H_2+H_4) ↔ 4.25 (H_{5exo}), 2.12 (H_{5endo}); 5.92 (H_2+H_4) ↔ 1.25 (H_{1endo}); 4.25 (H_{5exo}) ↔ 2.12 (H_{5endo}). Anal. calcd for $C_{13}H_{20}CoSiBF_4$: C, 44.60, H, 5.76; Found: C, 44.2112; H, 5.6916. Electrospray MS *m/z* calculated for $C_{13}H_{20}CoSi$ (M^+), 263.06608; Found: 263.06620.



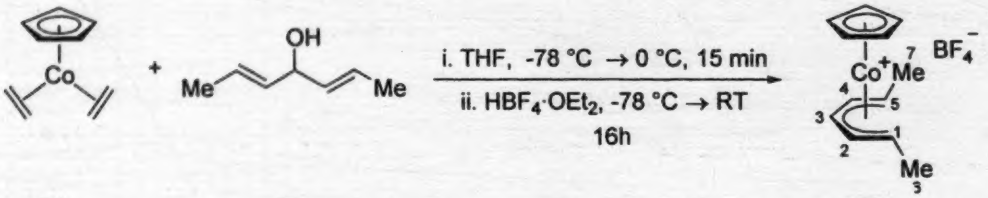
34 **59** **76**

[CpCo(η^5-3-methylhexadienyl)]$^+$BF$_4^-$ (76). Complex **76** (red powder, 105.2 mg, 0.3413 mmol, 55%) was prepared according to the detailed procedure given for complex **71** (starting bis[ethylene] **34**: 111.8 mg, 0.6206 mmol; dienol, 94.5 μL, 0.6827 mmol; HBF_4, 92 μL, 0.6827 mmol; 3-5 mL THF). Even after several recrystallization using pin-hole diffusion (dichloromethane/diethyl ether), the sample was not analytically pure. IR (microscope, cm^{-1}): 3116 (s), 1416 (s), 1284 (s), 1046 (br s), 865 (s). ^{1}H NMR (600 MHz, acetone-d_6): δ 7.11 (d, J = 7.2 Hz, 1H, H_3); 5.73 (s, 5H, Cp); 5.62 (ddd, J = 7.3 Hz, J = 9.9 Hz, J = 12.2 Hz, 1H, H_4); 4.18 (dd, J = 3.0 Hz, J = 9.6 Hz, 1H, H_{5exo}); 2.39 (s, 3H,

H_6); 2.37-2.40 (dd, J = 0.8 Hz, J = 12.0 Hz, 1H, H_{5endo}); 2.23 (q, J = 6.6 Hz, 1H, H_{1endo}); 1.75 (d, J = 6.6 Hz, 3H, H_7); GCOSY (500 MHz, acetone-d_6): δ 7.11 (H_3) ↔ 5.62 (H_4); 5.62 (H_4) ↔ 4.18 (H_{5exo}), 2.37-2.40 (H_{5endo}); 4.18 (H_{5exo}) ↔ 2.37-2.40 (H_{5endo}); 2.23 (H_{1endo}) ↔ 1.75 (H_7). ^{13}C APT NMR (100 MHz, acetone-d_6): δ 113.42 (+, C_2); 97.91 (-, C_3); 93.57 (-, C_4); 89.02 (-, Cp); 81.41 (-, C_1); 60.40 (+, C_5); 20.05 (-, C_6); [missing: 18.90 (C_7)]. ^{1}H-^{13}C gHSQC (599.93 MHz, acetone-d_6): δ 97.91 (C_3) ↔ 7.11 (H_3); 93.57 (C_4) ↔ 5.62 (H_4); 89.02 (Cp) ↔ 5.73 (Cp); 81.41 (C_1) ↔ 2.23 (H_1); 60.40 (C_5) ↔ 4.18 (H_{5exo}), 2.37-2.40 (H_{5endo}); 20.05(C_6) ↔ 2.39 (H_6); 18.90 (C_7) ↔ 1.75 (H_7); gHMBC (499.8 MHz, acetone-d_6): δ 113.42 (C_2) ↔ 2.39 (H_6), 1.75 (H_7); 97.91 (C_3) ↔ 2.37-2.40 (H_{5endo}); 81.41 (C_1) ↔ 2.39 (H_6), 1.75 (H_7). Anal. calcd for $C_{12}H_{16}CoBF_4$: C, 47.10; H, 5.27; Found: C, 45.2557; H, 5.2471. Electrospray MS *m/z* calculated for $C_{12}H_{16}Co$ (M^+), 219.05785; Found: 219.05786.



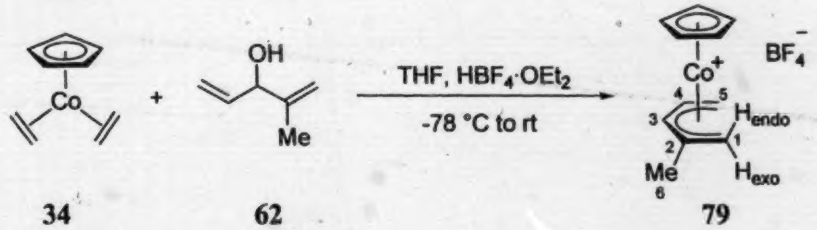
[CpCo(η^5-2-methylhexadienyl)]$^+$BF$_4^-$ (77). Complex **77** (red-brown solid, 20.15 mg, 0.06586 mmol, 34%) was prepared according to the detailed procedure given for complex **71** (starting bis[ethylene] **34**, 34.9 mg, 0.1937 mmol; dienol **60**: 23.9 mg, 27.8 μL, 0.2131 mmol; HBF_4, 28.8 μL, 0.2131 mmol; ~3 mL THF). Even after several recrystallization using pin-hole diffusion (dichloromethane/diethyl ether), the sample was not analytically pure. IR (microscope, cm^{-1}): 3120 (s), 1417 (s), 1284 (w), 1035 (br s), 1007 (s), 865 (s). ^{1}H NMR (acetone-d$_6$): δ 7.01 (dd, $^{3}J_{3\text{-}2}$ = 7.2 Hz, $^{4}J_{3\text{-}1endo}$ = 1.0 Hz, 1H, H$_3$), 5.70 (s, 5H, Cp), 5.63 (dd, $^{3}J_{2\text{-}3}$ = 7.3 Hz, $^{3}J_{2\text{-}1endo}$ = 11.8 Hz, 1H, H$_2$), 4.16 (m, 1H, H$_{5exo}$), 3.05 (dq, $^{3}J_{1endo\text{-}6}$ = 6.3 Hz, $^{3}J_{1endo\text{-}2}$ = 12.2 Hz, 1H, H$_{1endo}$), 2.30 (s, 3H, H$_7$), 1.71 (d, $^{3}J_{6\text{-}1endo}$ = 6.2 Hz, 3H, H$_6$), 1.67 (d, $^{3}J_{5endo\text{-}5exo}$ = 3.1 Hz, 1H, H$_{5endo}$); GCOSY (400 MHz, acetone-d$_6$): δ 7.02 (H$_3$) ↔ 5.70 (H$_2$); 4.16 (H$_{5exo}$) ↔ 1.67 (H$_{5endo}$); 3.05 (H$_{1endo}$) ↔ 1.71 (H$_6$); ^{13}C NMR (100 MHz, acetone-d$_6$): δ 113.85 (C$_4$); 95.70 (C$_3$); 95.27 (C$_2$); 89.07 (Cp); 85.47 (C$_1$); 58.85 (C$_5$); 25.55 (C$_7$); 22.82 (C$_6$); gHMQC (500 MHz, acetone-d$_6$): δ 95.70 (C$_3$) ↔ 7.02 (H$_3$); 89.07 (Cp) ↔ 5.70 (Cp); 58.85 (C$_5$) ↔ 4.16 (H$_{5exo}$), 1.67 (H$_{5endo}$); 25.55 (C$_7$) ↔ 2.30 (H$_7$); 22.82 (C$_6$) ↔ 1.71 (H$_6$) [missing C$_1$-H$_1$, C$_2$-H$_2$ correlations]; gHMBC (500 MHz, acetone-d$_6$): δ 113.85 (C$_4$) ↔ 2.32 (H$_7$); 95.70 (C$_3$) ↔ 2.32 (H$_7$); 95.27 (C$_2$) ↔ 1.71 (H$_6$); 85.47 (C$_1$) ↔ 1.71 (H$_6$); 58.85 (C$_5$) ↔ 2.32 (H$_7$). Electrospray MS *m/z* calculated for $C_{12}H_{16}Co$ (M$^+$), 219.05785; Found: 219.05798.


Co
+
OH
Me
Me
i. THF, -78 °C → 0 °C, 15 min
ii. HBF$_4$·OEt$_2$, -78 °C → RT
16h
Co$^+$
7
Me
BF$_4^-$
4
5
3
1
2
Me
5

34 **61** **78**

[CpCo(η^5-heptadienyl)]$^+$BF$_4^-$ (78). Complex **78** (dark red/black oily solid, yield unreported) was prepared according to the detailed procedure given for complex **71** (starting bis[ethylene] **34**, 300 mg, 1.705 mmol; dienol **61**: 210 mg, 1.876 mmol; HBF$_4$, 0.258 mL, 1.876 mmol; 3-5 mL THF). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.08 (t, $^{3}J_{HH}$ = 7.3

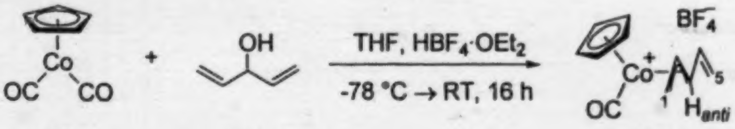
Hz, 1H, H_3), 5.57 (dd, $^3J_{HH}$ = 6.6 Hz, J = 11.2 Hz, 2H, H_2/H_4), 5.47 (s, 5H, Cp), 2.54 (dq, $^3J_{HH}$ = 6.3 Hz, J = 12.2 Hz, 2H, H_{1endo}/ H_{5endo}), 1.68 (d, $^3J_{HH}$ = 6.3 Hz, 6H, H_6/H_7); GCOSY (500 MHz, $CDCl_3$): δ 7.08 (H_3) ↔ 5.57 (H_2/H_4), 2.54 (H_{1endo}/ H_{5endo}); 2.54 (H_{1endo}/ H_{5endo}) ↔ 1.68 (H_6/H_7). The quantity of isolated compound **78** was insufficient for elemental analysis.



34 **62** **79**

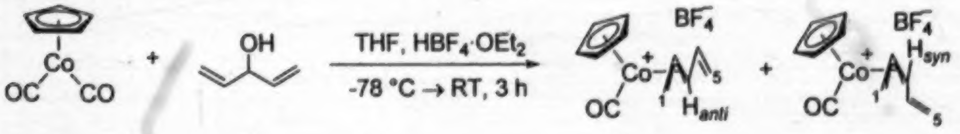
[CpCo(η^5-2-methylpentadienyl)]$^+$BF$_4^-$ (79). Complex **79** (red solid, 78.4 mg, 0.2686 mmol, 51%) was prepared according to the detailed procedure given for complex **71** (starting bis[ethylene] **34**: 94.8 mg, 0.5267 mmol; dienol: 58.1 mg, 0.5920 mmol; HBF_4, 81.5 μL, 0.5919 mmol; 3-5 mL THF). Crystals suitable for an X-ray diffraction analysis were grown from pin-hole diffusion (dichloromethane/diethyl ether) at room termperature. For full data on this crystal structure, request report # JMS0642 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}) 3121.0 (s), 3062.7 (w), 1515.0 (s), 1455.4 (s), 1430.3 (s), 1389.8 (s); 1287.2 (w), 1035.5 (br), 861.9 (s). ^1H NMR (400 MHz, acetone-d_6): δ 7.17 (d, J = 7.2 Hz, 1H, H_3); 5.86 (s, 5H, Cp); 5.80 (ddd, J = 7.2 Hz, J = 9.6 Hz, J = 12.0 Hz, 1H, H_4); 4.22-4.28 (m, 2H, H_{1exo}+H_{5exo}); 2.37 (s, 3H, H_6); 2.15 (dd, J = 2.6 Hz, J = 12.4 Hz, 1H, H_{5endo}); 1.67 (d, J = 3.2 Hz, 1H, H_{1endo}); GCOSY (400 MHz, acetone-d_6): δ 7.17 (H_3) ↔ 5.80 (H_4), 4.22-4.28 (H_{1exo}+H_{5exo}); 5.80 (H_4) ↔ 4.22-4.28 (H_{1exo}+H_{5exo}), 2.15 (H_{5endo}); 4.22-4.28 (H_{1exo}+H_{5exo}) ↔ 2.15 (H_{5endo}), 1.67 (H_{1endo}); ^{13}C NMR (100.7 MHz, acetone-d_6): δ 100.80 (C_3); 95.24 (C_4); 88.68 (Cp); 61.53 (C_5); 60.50 (C_1); 25.50 (C_6) [note: missing quaternary C_2]; gHSQC (599.93 MHz, acetone-d_6): δ 100.80 (C_3) ↔ 7.17 (H_3); 95.24 (C_4) ↔ 5.80 (H_4); 88.68 (Cp) ↔ 5.86 (Cp); 61.53 (C_5) ↔ 4.2 (H_{5exo}), 2.15 (H_{5endo}); 60.50 (C_1) ↔ 4.2 (H_{1exo}), 1.67 (H_{1endo}); 25.50 (C_7) ↔ 2.37 (H_6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.0 Hz, 1H, H_3); 5.78-5.85 (ddd, *J* = 7.6 Hz, *J* = 9.8 Hz, *J* = 12.1 Hz, 1H, H_4); 5.70 (s, 5H, Cp); 4.20 (dd, *J* = 2.9 Hz, *J* = 9.9 Hz, 1H, H_{5exo}); 4.08 (dd, 1H, H_{1exo}); 2.38 (s, 3H, H_6); 1.85 (dd, *J* = 2.6 Hz, *J* = 12.2 Hz, 1H, H_{5endo}); 1.35 (dd, 1H, H_{1endo}). Anal. calcd for $C_{11}H_{14}CoBF_4$: C, 45.25, H, 4.83; Found: C, 45.2563; H, 4.6491. Electrospray MS *m/z* calculated for $C_{11}H_{14}Co$ (M^+), 205.04220; Found: 205.04203.

Chapter Three Experimental Section



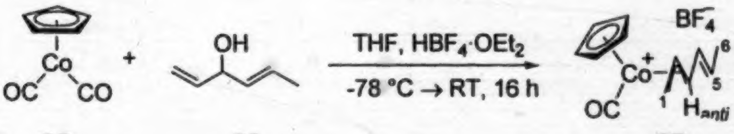
35 54 95

[CpCo(η^3-*syn*-pentadienyl)CO]$^+$$BF_4^-$ (95). In the drybox, starting complex **35** (100 mg, 0.5554 mmol) was dissolved in ~3 ml of THF in a Schlenk flask. Outside of the drybox, the reaction flask was cooled to -78 °C and the dienol (46.7 mg, 53.9 µL, 0.5558 mol) was added via microsyringe. After 10-15 minutes of stirring, the acid (76.6 µL, 0.5554 mmol) was added dropwise via microsyringe. The reaction was allowed to warm slowly to RT over 16h. Solvents were then removed *in vacuo* and the reaction flask taken into the drybox. Diethyl ether (15-30 mL) was added to triturate product and the ether removed via pipette and then *in vacuo*. The orange, red powder (133.0 mg, 97%) was characterized by ^{1}H NMR and MS, yet could not be purified to analytical purity due to trace amounts of CpCo(η^5-pentadienyl) complex **71** and cobaltacenium. ^{1}H NMR (400 MHz, acetone-d_6) δ 6.67 (1H, dt, J = 10.3 Hz, J = 16.8 Hz, 1H, H_4), 6.04 (overlap with Cp, m, 1H, H_{5syn}), 5.99 (s, 5H, Cp), 5.92 (m, 1H, H_2), 5.74 (ddd, J = 1.1, J = 1.8 Hz, J = 9.7 Hz, 1H, H_{5anti}), 4.58 (ddd, J = 0.6 Hz, J = 1.4 Hz, J = 7.1 Hz, 1H, H_{1syn}), 4.42 (dd, J = 10.8 Hz, J = 11.4 Hz, 1H, H_3), 2.71 (ddd [app dt], J = 1.2 Hz, J = 12.3 Hz, 1H, H_{1anti}); GCOSY (400 MHz, acetone-d_6) 6.67 (H_4) ↔ 6.04 (H_{5syn}), 5.74 (H_{5anti}); 5.92 (H_2) ↔ 4.58 (H_{1syn}), 2.71 (H_{1anti}); ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.55 (app dt, J = 10.0 Hz, J = 16.6 Hz, 1H, H_4), 6.04 (app dt, J = 7.2 Hz, J = 12.1 Hz, 1H, H_{5syn}), 5.94 (d, J = 16.8 Hz, 1H, H_{5anti}), 5.82 (d, J = 10.1 Hz, 1H, H_2), 5.78 (s, 5H, Cp), 4.65 (d, J = 5.5 Hz, 1H, H_{1syn}), 3.96 (dd, J = 11.0 Hz, J = 11.4 Hz, 1H, H_3), 2.42 (1H, d, J = 12.3 Hz, 1H, H_{1anti}). Electrospray MS *m/z* calculated for $C_{11}H_{12}OCo$ (M$^+$): 219.02146; Found, 219.02140. Anal. calcd for $C_{11}H_{12}OCoBF_4$: C, 43.18; H, 3.95; Found: C, 42.7855; H, 4.34.



35 **54** **95** **96**

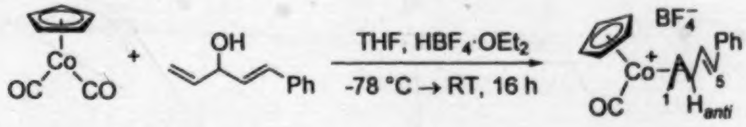
[CpCo(η^3-*syn*-pentadienyl)CO]$^+$BF$_4^-$ (95) and [CpCo(η^3-*anti*-pentadienyl)CO]$^+$BF$_4^-$ (96). In the drybox, dicarbonyl complex **35** (50 mg, 0.2777 mmol) was dissolved in 3 mL of THF in a Schlenk flask. Outside of the drybox, the reaction flask was cooled to -78 °C and the dienol (23.4 mg, 27.1 µL, 0.2777 mmol) was added via microsyringe. After 10-15 minutes of stirring, the acid (38.3 µL, 0.2777 mmol) was added dropwise via microsyringe. The reaction was allowed to stir for 15 min at -78 °C. The cooling bath was then removed and allowed to warm quickly to RT over 3 h. Solvents were then removed *in vacuo* and the reaction flask taken into the drybox. Diethyl ether (15-30 mL) was added to triturate product and the ether removed via pipette and then *in vacuo*. The bright red product mixture (71 : 29, *syn*/*anti*) was characterized by ^{1}H NMR, yet could not be purified to analytical purity due to trace amounts of CpCo(η^5-pentadienyl) complex **71** and cobaltacenium. ***Anti*-isomer**: IR (microscope, cm^{-1}): 3120 (w), 2941 (w), 2857 (w), 2079 (s), 2021 (w), 1961 (w), 1442 (w), 1411 (w), 1074 (s), 863 (m); ^{1}H NMR (500 MHz, acetone-d$_6$) δ 6.30 (dt, $J_{4\text{-}3/5anti}$ = 10.3 Hz, $J_{4\text{-}5syn}$ = 17.0 Hz, 1H, H$_4$), 6.08 (t, 1H, H$_{5syn}$), 5.98 (overlap with Cp, m, 1H, H$_2$), 5.90 (s, 5H, Cp), 5.72 (overlap with syn-isomer, m, 1H, H$_{5anti}$), 5.07 (d, J = 17.0 Hz, 1H, H$_{1syn}$), 4.92 (d, J = 10.1 Hz, 1H, H$_3$), 2.19 (m, 1H, H$_{1anti}$).



35 **55** **97**

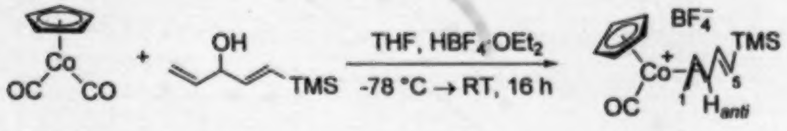
[CpCo(η^3-*syn*-1-methylpentadienyl)CO]$^+$BF$_4^-$ (97). Complex **97** (dark red powder, 121 mg, 83%) was prepared according to the detailed procedure given for complex **95** (dicarbonyl complex **35**, 100 mg, 0.56 mmol; dienol **55**, 54.5 mg, 0.56 mmol; HBF$_4$, 76.5 µL, 0.56 mmol; ~1 mL THF). IR (microscope, cm^{-1}): 3515 (br s), 3124 (s), 2964 (m), 2075 (s), 1633 (s), 1521 (w), 1444 (m), 1412 (m), 1381 (m), 1287 (m), 1109 (br s), 865 (s), 765 (s); ^{1}H NMR (400 MHz, acetone-d$_6$): δ 6.63 (dq, J = 7.0 Hz, J = 15.0 Hz, 1H, H$_{5anti}$), 6.47 (ddq, J = 14.0 Hz, J = 10.6 Hz, J = 1.5 Hz, 1H, H$_4$), 5.96 (s, 5H, Cp), 5.89

(dt, J = 7.1 Hz, J = 12.0 Hz, 1H, H_2), 4.54 (t, J = 11.2 Hz, 1H, H_3), 4.52 (overlap with H_3, m, 1H, H_{1syn}), 2.60 (dt, J = 12.2 Hz, J = 1.0 Hz, 1H, H_{1anti}), 1.68 (dd, J = 1.4 Hz, J = 6.9 Hz, 3H, H_{5synMe}). Electrospray MS attempted, but no molecular ion was detected.



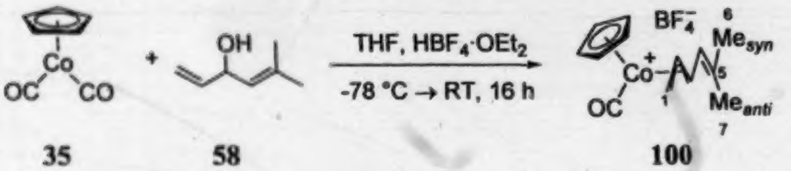
35 **56** **98**

CpCo(η^3-*syn*-1-phenylpentadienyl)CO]$^+$$BF_4^-$ (98). Complex **98** (bright red powder, 145.5 mg, 38 %) was prepared according to the detailed procedure given for complex **95** (dicarbonyl complex **35**, 180 mg, 1.00 mmol; dienol **55**, 160 mg, 1.00 mmol; HBF4, 5-6 mL THF). IR (microscope, cm^{-1}): 3529 (br m), 3121 (m), 3058 (w), 2945 (w), 2058 (s), 2019 (m), 1610 (s), 1576 (m), 1511 (m), 1459 (m), 1443 (m), 1411 (m), 1168 (m), 1033 (br s), 858 (s), 750 (s), 687 (s); ^{1}H NMR (300 MHz, acetone-d_6) δ 7.68 (dd, J = 2.2 Hz, J = 7.5 Hz, 2H, Ph), 7.4 (m, 3H, Ph), 7.32 (d, J = 10.5 Hz, 1H, H_5), 7.27 (d, J = 10.5 Hz, 1H, H_4), 6.10 (dt, J = 7.2 Hz, J = 12.0 Hz, H_2), 6.01 (s, 5H, Cp), 4.74 (dd, J = 10.9 Hz, J = 10.8 Hz, 1H, H_3), 4.59 (ddd, J = 7.1 Hz, J = 1.4 Hz, J = 0.5 Hz, 1H, H_{1syn}), 2.72 (dq, J = 12.2 Hz, 1H, H_{1anti}); GCOSY (300 MHz, acetone-d_6) δ 7.68 (Ph) ↔ 7.4 (Ph); 7.32 (H_5) ↔ 7.27 (H_4); 7.27 (H_4) ↔ 4.74 (H_3); 6.10 (H_2) ↔ 4.74 (H_3), 4.59 (H_{1syn}), 2.72 (H_{1anti}); 4.59 (H_{1syn}) ↔ 2.72 (H_{1anti}). Electrospray MS *m/z* calculated for $C_{17}H_{16}OCo$ (M^+): 295.05276; Found, 295.05270.

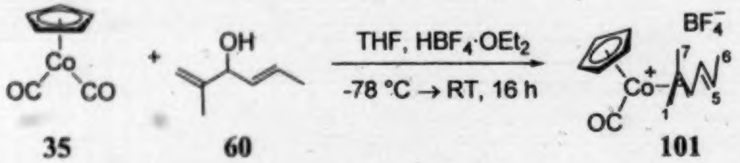


35 **57** **99**

CpCo(η^3-*syn*-1-trimethylsilylpentadienyl)CO]$^+$BF$_4^-$ (99). Complex **99** (orange powder, 733 mg, 70 %) was prepared according to the detailed procedure given for complex **95** (dicarbonyl complex **35**: 500 mg, 2.78 mmol; dienol **55**: 434 mg, 2.78 mmol; HBF$_4$, 421 µL, 2.78 mmol; 5 mL THF). Crystals suitable for an X-ray diffraction analysis were grown from pin-hole diffusion (nitromethane/diethyl ether) at room temperature. For full data on this crystal structure, request report # JMS0723 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}): 3524 (br m), 3119 (m), 2954 (m), 2864 (m), 2081 (s), 1628 (m), 1443 (m), 1408 (m), 1262 (m), 1249 (m), 1028 (br s), 839 (s); ^{1}H NMR ^{1}H NMR (500 MHz, acetone-d$_6$) δ 6.84 (m, 2H, H$_4$+H$_5$), 6.02 (dt, *J* = 12.0 Hz, *J* = 7.0 Hz, 1H, H$_2$), 5.98 (s, 5H, Cp), 4.60 (ddd, *J* = 0.6 Hz, *J* = 1.4 Hz, *J* = 7.1 Hz, 1H, H$_{1syn}$), 4.38 (dd, *J* = 9.0 Hz, *J* = 11.6 Hz, 1H, H$_3$), 2.74 (dt, *J* = 1.0/1.3 Hz, *J* = 12.3 Hz, 1H, H$_{1anti}$), 0.13 (s, 9H, s, H$_{5anti\text{-}SiMe3}$); GCOSY (500 MHz, acetone-d$_6$) 6.84 (H$_4$+H$_5$) ↔ 4.38 (H$_3$); 6.12 (H$_2$) ↔ 4.60 (H$_{1syn}$), 4.38 (H$_3$), 2.74 (H$_{1anti}$); 4.60 (H$_{1syn}$) ↔ 2.74 (H$_{1anti}$); 4.38 (H$_3$) ↔ 2.74 (H$_{1anti}$). Electrospray MS *m/z* calculated for C$_{14}$H$_{20}$OSiCo (M$^+$): 291.06099; Found, 291.06064. The quantity of purified compound **99** was insufficient for elemental analysis.

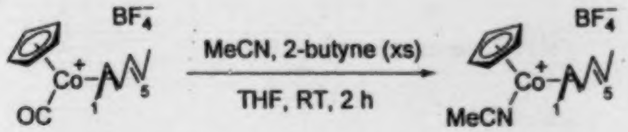

Co
OC
CO
+
OH
THF, HBF4·OEt2
-78 °C → RT, 16 h
BF4−
Co+
OC
1
5
6
Mesyn
Meanti
7
35
58
100

CpCo(η^3-*syn*-2-methylhexadienyl)CO]$^+$BF$_4^-$ (100). Complex **100** (red-orange powder, 389 mg, 42 %) was prepared according to the detailed procedure given for complex **95** (dicarbonyl complex **35**: 500 mg, 2.78 mmol; dienol **55**: 312 mg, 2.78 mmol; HBF$_4$, 421 µL, 2.78 mmol; 5 mL THF). ^{1}H NMR (300 MHz, acetone-d$_6$) δ 9.18 (m, 1H, Pyr), 8.80 (m, 0.5H, Pyr), 8.35 (m, 1H, Pyr), 6.24 (d, *J* = 10.7 Hz, 1H, H_2), 5.96 (m, 1H, H_4); 5.90 (s, 5H, Cp) , 4.66 (t, *J* = 11.4 Hz, 1H, H_3), 4.48 (d, *J* = 6.9 Hz, 1H, H_{5syn}), 2.58 (d, *J* = 12.2 Hz, 1H, H_{5anti}), 1.80 (s, 3H, H_{1synMe}), 1.75 (s, 3H, $H_{1antiMe}$). Electrospray MS attempted, but no molecular ion detected.


Co
OC
CO
+
OH
THF, HBF4·OEt2
-78 °C → RT, 16 h
BF4−
Co+
OC
1
5
6
7
35
60
101

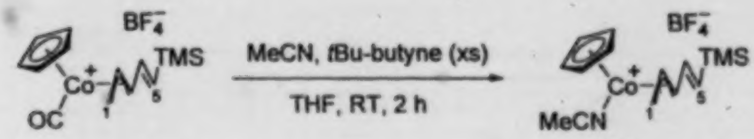
CpCo(η^3-*syn*-4-methylhexadienyl)CO]$^+$BF$_4^-$ (101). Complex **101** (light orange powder, 213 mg, 11 %) was prepared according to the detailed procedure given for complex **95** (dicarbonyl complex **35**: 1.0 g, 5.56 mmol; dienol **55**: 0.799 mL, 6.12 mmol; HBF$_4$, 0.843 mL, 6.12 mmol; 10 mL Et$_2$O). By NMR spectroscopy, the reaction mixture contained cobaltocenium by-product. ^{1}H NMR (300 MHz, acetone-d$_6$): δ 6.65 (m, 1H, H_4 [?]); 6.39 (ddd, *J* = 0.9 Hz, *J* = 7.3 Hz, *J* = 10.8 Hz, 1H, H_2 [?]); 5.95 (s, 5H, Cp); 4.45 (dd, *J* = 1.5 Hz, *J* = 19.8 Hz, 1H, H_3 [?]); 4.37 (dd, *J* = x Hz, *J* = x Hz, 1H, H_{1syn}); 2.54

(d, *J* = 11.6 Hz, 3H, H_{1anti}); 1.79 (dd, *J* = 1.8 Hz, *J* = 7.2 Hz, 3H, H_{6synMe}); 1.74 (d, *J* = 5.6 Hz, 3H, $H_{7antiMe}$). Electrospray MS attempted, but no molecular ion detected.



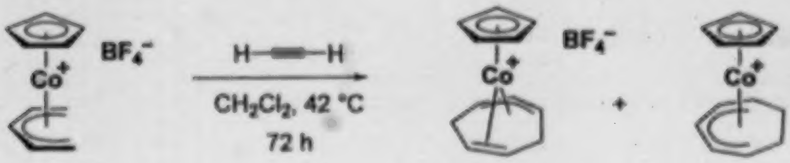
97 **103**

[CpCo(η^3-*syn*-hexadienyl)acetonitrile]$^+$BF$_4^-$ (103). Complex **97** (30 mg, 0.1028 mmol) was dissolved in 3-5 mL of THF in a Schlenk flask in the dry box and then removed to the Schlenk line. Excess 2-butyne (80.4 µL, 1.028 mmol) was then added via microsyringe and 1 equiv. of acetonitrile (5.4 µL, 0.1028 mmol) was added to the reaction flask. After two hours, solvents were removed *in vacuo* and the reaction mixture was purified by column chromatography (3% MeOH/CH_2Cl_2). A non-polar by-product was not isolated, however a red solution was collected, evaporated and characterized. The reaction mixture contained (by NMR spectroscopy) unreacted carbonyl complex **97**, η^5-pentadienyl complex **72**, and acetonitrile complex **103**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (dq, 1H, H_{5anti}), 6.32 (dd, 1H, H_4), 5.89 (ddd, 1H, H_2), 5.75 (s, 5H, Cp), 4.52 (dd, 1H, H_{1syn}), 4.20 (t, 1H, H_3), 2.31 (dd, 1H, H_{1anti}), 1.76 (overlapping with H_6 of η^5-1methylpentadienyl, s, 3H, H_6); GCOSY (400 MHz, $CDCl_3$): δ 6.53 (H_{5anti}) ↔ 6.32 (H_4), 1.76 (H_6); 5.89 (H_2) ↔ 4.56 (H_{1syn}), 2.31 (H_{1anti}).



99 **104**

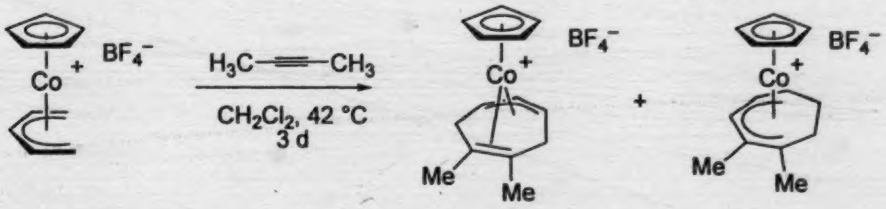
[CpCo(η^3-*syn*-1-trimethylsilylpentadienyl)acetonitrile]$^+$BF$_4^-$ (104). Complex **99** (30 mg, 0.07934 mmol) was dissolved in 3-5 mL of THF in a Schlenk flask in the dry box. Then excess 3, 3-dimethyl-1-butyne (65.1 mg, 0.7934 mmol) was added and stirred for 10 min. Next an excess of acetonitrile (32.6 mg, 41.5 µL, 0.7934 mmol) was slowly added to the reaction flask. After two hours, solvents were removed *in vacuo* and the reaction mixture was removed from the dry box and purified by column chromatography (3% MeOH/CH_2Cl_2). The non-polar by-product was not isolated, but a red solution was collected, evaporated and characterized. The product was obtained in addition to decarbonylated η^5-pentadienyl complex **74** (~ 3 : 1). The same reaction mixture was obtained when the reaction was repeated with both excess acetylene and excess trimethylsilylacetylene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, 1H, H_{5anti}), 6.68 (dd, 1H, H_4), 6.07 (m, 1H, H_2), 5.80 (s, 5H, Cp), 4.74 (d, 1H, H_{1syn}), 4.02 (t, 1H, H_3), 2.51 (d, 1H, H_{1anti}), 1.70 (br s, 1H, $C\underline{H}_3CN$-), 0.20 (9H, s, -$SiC\underline{H}_3$); GCOSY (400 MHz, $CDCl_3$) δ 6.84 (H_{5anti}) ↔ 6.68 (H_4); 6.68 (H_4) ↔ 4.02 (H_3); 6.07 (H_2) ↔ 4.76 (H_{1syn}), 2.52 (H_{1anti}).



71 126 127

[CpCo(η^2,η^3-cycloheptadienyl)]$^+$BF$_4^-$ (126) and [CpCo(η^5-cycloheptadienyl)]$^+$BF$_4^-$ (127). η^5-Pentadienyl complex **71** (100 mg, 0.3601 mmol) was dissolved in CH_2Cl_2 (3 mL) and placed in a glass reaction bomb. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test-tube for 20 minutes in order to ensure saturation. Then, ~2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and heated to 60 °C over 24 hours. The solution turned from orange to red. The solvent was then removed *in vacuo* and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried providing 68.4 mg (63%) of product as a dark, red powder. The ^{1}H NMR spectrum showed that this was a mixture of η^3,η^2-isomer and fully-conjugated η^5-isomer present (24 : 76). **η^5 isomer**: ^{1}H NMR (400 MHz, acetone-d$_6$): δ 7.41 (t, 1H, H_3), 5.80 (dt, 2H, H_2/H_4), 5.78 (overlap with H_2/H_4, s, 5H, Cp), 5.60 (m, 2H, H_1/H_5), 2.49 (dd, 2H, H_{6endo}/H_{7endo}), 1.25 (d, 2H, H_{6exo}/H_{7exo}); GCOSY (400 MHz, acetone-d$_6$): δ 7.41 (H_3) ↔ 5.80 (H_2/H_4); 5.80 (H_2/H_4) ↔ 5.60 (H_1/H_5); 5.60 (H_1/H_5) ↔ 2.49 (H_{6endo}/H_{7endo}), 1.25 (H_{6exo}/H_{7exo}); 2.49 (H_{6endo}/H_{7endo}) ↔ 1.25 (H_{6exo}/H_{7exo}). **η^3,η^2-isomer**: ^{1}H NMR (400 MHz, acetone-d$_6$): δ 5.10 (m, 2H, H_1/H_3), 4.08 (t, 1H, H_2), 3.80 (m, 2H, H_6/H_7), 3.15 (m, 2H, H_{4exo}/H_{7exo}), 2.30 (dd, 2H, H_{4endo}/H_{7endo}); GCOSY (400 MHz, acetone-d$_6$): δ 5.10 (H_1/H_3) ↔ 4.08 (H_2), 3.15

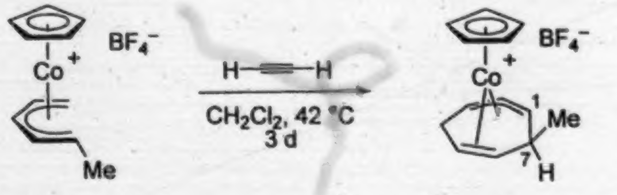
(H_{4exo}/H_{7exo}), 2.30 (H_{4endo}/H_{7endo}); 4.08 (H_2) ↔ 3.15 (H_{4exo}/H_{7exo}), 2.30 (H_{4endo}/H_{7endo}); 3.80 (H_5/H_6) ↔ 3.15 (H_{4exo}/H_{7exo}), 2.30 (H_{4endo}/H_{7endo}); 3.15 (H_{4exo}/H_{7exo}) ↔ 2.30 (H_{4endo}/H_{7endo}). **Isomeric mixture**: IR (microscope, cm^{-1}): 3479 (br), 3119 (s), 2934 (w), 2856 (w), 1709 (w), 1418 (s), 1286 (m), 1054 (br s), 867 (s). Electrospray MS *m/z* calculated for $C_{12}H_{14}Co$ (M^+), 217.04220; Found: 217.04219.



71 **128** **129**

[CpCo(η^2,η^3-1,2-dimethylcycloheptadienyl)]$^+$BF$_4^-$ (128) and [CpCo(η^5-1,2-dimethylcycloheptadienyl)]$^+$BF$_4^-$ (129). A glass reaction bomb was charged with a solution of 71 (100 mg, 0.3601 mmol) in dichloromethane (~ 3 mL). An aliquot of 2-butyne (282 μL, ~3.601 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. Two deep red fractions were collected and, upon removal of solvent, the first fraction proved to be a mixture of the allyl-olefin product and an unknown by-product (1 : 2) and the second fraction was the starting material.

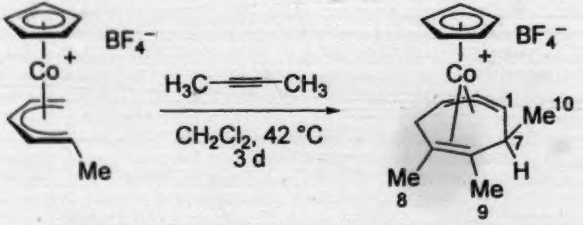
The above procedure was repeated with heating to 65 °C for 72 hours, isolating a single red fraction from column chromatography to provide 66.8 mg (56%) of total product as a red powder. By NMR spectroscopy, this fraction contained a mixture of the fully conjugated product **129** and an unknown by-product (1 : 3). Neither silica gel column chromatography nor pin-hole diffusion crystallization (ether into dichloromethane) achieved further separation of the two compounds. **η^3,η^2-isomer**: ^{1}H NMR (400 MHz, acetone-d_6): δ 5.45 (s, 5H, Cp); 5.40 (ddd, 2H, H_1/H_3); 4.20 (t, 1H, H_2); 3.11 (dd, 2H, H_{4endo}/H_{7endo}); 2.67 (dd, 2H, H_{4exo}/H_{7exo}); 2.20 (s, 3H, H_8/H_9); GCOSY (400 MHz, acetone-d_6): δ 5.40 (H_1/H_3) ↔ 4.20 (H_2), 3.11 (H_{4endo}), 2.67 (H_{4exo}); 3.11 (H_{4endo}) ↔ 2.67 (H_{4exo}). **η^5-isomer (A)**: ^{1}H NMR (400 MHz, acetone-d_6): δ 7.17 (d, $J_{2\text{-}3}$ = 7.3 Hz, 1H, H_3), 5.65 (m, 1H, H_2), 5.57 (s, 5H, Cp), 5.23 (ddd, $J_{1\text{-}2}$ = 9.1 Hz, $J_{1\text{-}7endo}$ = 7.5 Hz, $J_{1\text{-}3}$ = 1.5 Hz, 1H, H_1), 3.19 (dddd, $J_{7endo\text{-}7exo}$ = 19.9 Hz, $J_{7endo\text{-}6exo}$ = 11.7 Hz, $J_{7endo\text{-}1}$ = 7.7 Hz, $J_{7endo\text{-}6endo}$ = 3.5 Hz, 1H, H_{7endo}), 2.45 (s, 3H, H_8), 2.05 (m, 1H, H_{7exo}), 1.84 (s, 3H, H_9), 1.50 (ddt, $J_{6endo\text{-}6exo}$ = 12.3 Hz, $J_{6endo\text{-}7endo}$ = 7.7 Hz, $J_{6endo\text{-}7exo/9}$ = 1.5 Hz, 1H, H_{6endo}), 0.32 (dt, $J_{6exo\text{-}6endo/7exo}$ = 12.4 Hz, $J_{6exo\text{-}7exo}$ = 5.3 Hz, 1H, H_{6exo}); GCOSY (400 MHz, acetone-d_6): δ 7.17 (H_3) ↔ 5.23 (H_1), 2.45 (H_8), 1.84 (H_9); 5.65 (H_2) ↔ 5.23 (H_1), 3.19 (H_{7endo}), 2.05 (H_{7exo}), 1.50 (H_{6endo}); 5.23 (H_1) ↔ 2.05 (H_{7exo}); 3.19 (H_{7endo}) ↔ 2.05 (H_{7exo}), 1.50 (H_{6endo}), 0.32 (H_{6exo}); 2.05 (H_{7exo}) ↔ 0.32 (H_{6exo}); 1.50 (H_{6endo}) ↔ 0.32 (H_{6exo}). **Unknown by-product (B)**: ^{1}H NMR (400 MHz, acetone-d_6): δ 7.37 (d, J = 5.4 Hz, 1H, Hx), 5.65 (s, 5H, Cp), 5.59 (m, 1H, Hx), 3.83 (d, 1H, Hx), 2.20 (s, 3H, Hx), 1.63 (d, J = 12.5 Hz, 8H, Hx); GCOSY (500 MHz, acetone-d_6): δ 7.37 (Hx) ↔ 5.59 (Hx), 3.83 (Hx), 2.20 (Hx), 1.63 (Hx); 5.59 (Hx) ↔ 3.83 (Hx), 2.20 (Hx), 1.63 (Hx); 3.83 (Hx), ↔ 1.63 (Hx). **Mixture of the compounds A and B**: IR (microscope, cm^{-1}): 3113 (w), 2976 (w), 2942 (w), 2883 (w), 2835 (w), 1699 (w), 1458 (w), 1432 (w), 1411 (w), 1388 (w), 1285 (w), 1250 (w), 1055 (br s), 856 (w). ^{13}C NMR (125 MHz, acetone-d_6): δ 111.0, 108.0, 107.9, 99.1, 91.9, 91.2, 90.4, 89.1, 87.8, 87.6 (Cp?), 87.2, 86.9, 70.0, 55.7, 41.1, 33.8, 27.6, 20.4, 18.9, 18.4, 17.3, 11.8, 10.4. gHMQC (500 MHz, acetone-d_6): δ 99.3 ↔ 7.18 (B, H2), 92.0 ↔ 7.36 (A, H2), 87.6 ↔ 5.65 (A), 89.2 ↔ 5.56 (B), 55.9 ↔ 3.84 (B), 33.90 ↔ 1.61 (B), 27.6 ↔ 1.84 (A, Me), 19.0 ↔ 1.62, 18.3 ↔ 2.15 (A), 17.4 ↔ 1.67, 17.1 ↔ 1.60. Electrospray MS *m/z* calculated for $C_{14}H_{18}Co$ (M^+), 245.07350; Found: 245.07387.



72 **130**

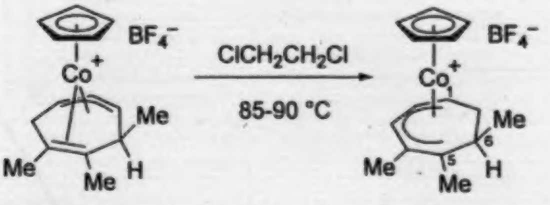
[CpCo(η^3,η^2-1-*endo*-methylcycloheptadienyl)]$^+$BF$_4^-$ (130). Complex **72** (100 mg, 0.3425 mmol) was dissolved in CH_2Cl_2 (3 mL) and placed in a reaction bomb. Simultaneously, acetylene was bubbled through CH_2Cl_2 in a test-tube for 20 minutes in order to ensure saturation. Then, ~2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at 40 °C over 3 days. The solvent was then removed *in vacuo* and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The dark-red fraction was collected and dried providing 59.7 mg 55%) of total product as a dark, red powder. By ^{1}H NMR spectroscopy, this fraction contained η^3,η^2-isomer **130** with a small quantity of cobaltocenium by-product as well as an unidentified fully-conjugated η^5 by-product (the fully-conjugated by-product likely corresponds to the double alkyne [5+2+2] addition product in the HRMS). Crystals suitable for an X-ray diffraction analysis were grown from pin-hole diffusion (dichloromethane/diethyl ether) at room temperature. For full data on this crystal structure, request report # JMS0585 from the Structure Determination Laboratory at the University of Alberta Department of Chemistry. IR (microscope, cm^{-1}): 3401 (w), 3116

(w), 2936 (w), 2860 (w), 1636 (w), 1416 (s), 1299 (w), 1284 (w), 1054 (br s), 867 (s). ^{1}H NMR (400 MHz, acetone-d$_6$): δ 5.75 (s, 5H, Cp); 5.10 (m, 1H, H$_3$); 4.70 (m, 1H, H$_1$); 4.10 (t, 1H, H$_2$); 3.85 (dd, 1H, H$_5$); 3.39 (m, 1H, H$_6$); 3.12 (m, 1H, H$_{4endo}$); 2.55 (m, 1H, H$_{7exo}$); 2.28 (m, 1H, H$_{4exo}$); 1.53 (d, 3H, H$_{8endoMe}$); GCOSY (400 MHz, acetone-d$_6$): δ 5.10 (H$_3$) ↔ 4.10 (H$_2$), 3.12 (H$_{4endo}$), 2.28 (H$_{4exo}$); 4.70 (H$_1$) ↔ 4.10 (H$_2$), 2.55 (H$_{7exo}$); 3.85 (H$_5$) ↔ 3.39 (H$_6$), 3.12 (H$_{4endo}$), 2.28 (H$_{4exo}$); 3.39 (H$_6$) ↔ 2.55 (H$_{7exo}$); 3.12 (H$_{4endo}$) ↔ 2.28 (H$_{4exo}$); 2.55 (H$_{7exo}$) ↔ 1.53 (H$_{8endoMe}$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.61 (s, 5H, Cp); 5.04 (ddd, 1H, H$_3$); 4.58 (dd, J = 3.7 Hz, J = 7.3 Hz, 1H, H$_1$); 4.01 (t, J = 7.5 Hz, 1H, H$_2$), 3.73 (dd, J = 7.0 Hz, 1H, H$_5$); 3.14-3.24 (m [t (J = 5.4) +dd], 2H, H$_6$+H$_{4endo}$); 2.39 (dd, 1H, H$_{7exo}$); 2.14 (dd, 1H, H$_{4exo}$); 1.52 (d, 3H, H$_{8endoMe}$); GCOSY (400 MHz, CDCl$_3$): δ 5.04 (H$_3$) ↔ 4.01 (H$_2$), 3.14 (H$_{4endo}$), 2.14 (H$_{4exo}$); 4.58 (H$_1$) ↔ 4.01 (H$_2$), 2.39 (H$_{7exo}$); 3.73 (H$_5$) ↔ 3.24 (H$_6$); 3.24 (H$_6$) ↔ 2.39 (H$_{7exo}$); 3.14 (H$_{4endo}$) ↔ 2.14 (H$_{4exo}$); 2.39 (H$_{7exo}$) ↔ 1.52 (H$_{8endoMe}$). Electrospray MS *m/z* calculated for C$_{13}$H$_{16}$Co (M$^+$), 231.05785; Found: 231.05809.



72 **132**

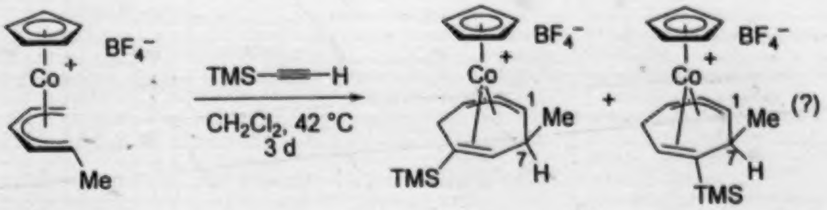
[CpCo(η^3,η^2-1-*endo*-2,3-trimethylcycloheptadienyl)]$^+$BF$_4^-$ (132). A glass reaction bomb was charged with a solution of **72** (100 mg, 0.3425 mmol) in dichloromethane (~ 3 mL). An aliquot of 2-butyne (~268 μL, 3.425 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, which was comprised primarily of the desired product but contained traces (less than 5% each by ^{1}H NMR integration) of minor impurities. Analytically pure **132** (51 mg, 43%) was obtained using pin-hole diffusion crystallization (dichloromethane/diethyl ether). IR (microscope, cm^{-1}): 3388 (br), 3113 (w), 2972 (w), 1709 (w), 1522 (w), 1468 (m), 1435 (m), 1412 (m), 1382 (m), 1300 (w), 1053 (br s), 858 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.36 (m [overlapping with Cp], 1H, H_3); 5.32 (s, 5H, Cp); 4.79 (dd, J = 4.5 Hz, J = 6.7 Hz, 1H, H_1); 4.15 (t, J = 7.3 Hz, 1H, H_2); 3.14 (dd, J = 9.3 Hz, J = 14.1 Hz, 1H, H_{4endo}); 2.58 (t, J = 5.8 Hz, 1H, H_{7exo}); 2.53 (dd, J = 4.4 Hz, J = 14.1 Hz, 1H, H_{4exo}); 2.04 (s, 3H, H_{8Me}); 1.84 (s, 3H, H_{9Me}); 1.54 (d, J = 7.0 Hz, 3H, $H10_{endoMe}$); ^{1}H NMR (400 MHz, acetone-d$_6$): δ 5.48 (s, 5H, Cp); 5.32 (ddd, 1H, H_3); 4.86 (ddd, 1H, H_1); 4.14 (t, J = 7.3 Hz, 1H, H_2); 3.12 (dd, J = 9.3 Hz, J = 14.2 Hz, 1H, H_{4endo}); 2.70 (t, J = 6.2 Hz, 1H, H_{7exo}); 2.63 (dd, J = 4.6 Hz, J = 14.0 Hz, 1H, H_{4exo}); 2.09 (s, 3H, H_{8Me}); 1.92 (s, 3H, H_{9Me}); 1.52 (d, J = 7.0 Hz, 3H, $H_{10endoMe}$); GCOSY (300 MHz, acetone-d$_6$): δ 5.32 (H_3) ↔ 4.14 (H_2), 3.12 (H_{4endo}); 4.86 (H_1) ↔ 4.14 (H_2); 3.12 (H_{4endo}) ↔ 2.63 (H_{4exo}); 2.70 (H_{7exo}) ↔ 1.52 ($H_{10endoMe}$); ^{13}C NMR (100 MHz, acetone-d$_6$): δ 88.96 (Cp); 88.93 (C_3); 88.85 (C_2); 48.96 (C_1); 32.05 (C_7); 31.39 (C_4); 23.70 (C_8); 17.98 (C_{10}); 16.00 (C_9). gHSQC (400 MHz, acetone-d$_6$): δ 88.96 (Cp) ↔ 5.48 (Cp); 88.85 (C_2) ↔ 4.14 (H_2); 48.96 (C_1) ↔ 4.86 (H_1); 32.05 (C_7) ↔ 2.70 (H_{7exo}); 31.39 (C_4) ↔ 3.12 (H_{4endo}), 2.63 (H_{4exo}); 23.70 (C_8) ↔ 2.09 (H_8); 17.98 (C_{10}) ↔ 1.52 (H_{10}); 16.00 (C_9) ↔ 1.92 (H_9) [missing correlation: 88.93 (C_3) ↔ 5.32 (H_3)]. Anal. calcd for $C_{15}H_{20}CoBF_4$: C, 52.06, H, 5.83; Found: C, 51.7911; H, 5.7621. Electrospray MS *m/z* calculated for $C_{15}H_{20}Co$ (M^+), 259.08915; Found: 259.08941.



132 **133**

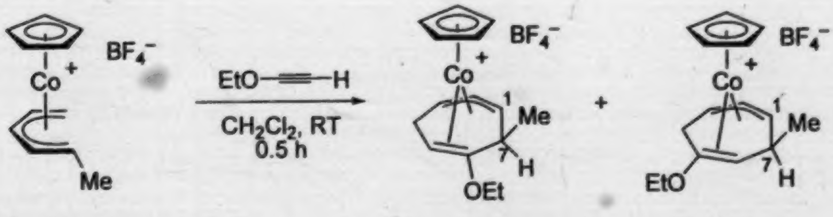
[CpCo(η^5-1-*endo*-2,3-trimethylcycloheptadienyl)]$^+$BF$_4^-$ (133). A glass reaction bomb was charged with a solution of **132** (100 mg, 0.2890 mmol) in dichloroethane (~ 4 mL). The bomb was sealed, and the solution was maintained at 85-90 °C for 24 h. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, was quantitative sample comprised primarily of the desired product but contained traces (less than 5% each by ^{1}H NMR integration) of minor impurities. IR (microscope, cm-1): 3115 (m), 2973 (m), 2880 (m), 1474 (s), 1431 (s), 1413 (s), 1012 (s), 857 (s). ^{1}H NMR (500 MHz, acetone-d$_6$): δ 7.21 (d, $J_{3\text{-}2}$ = 7.2 Hz, 1H, H_3); 5.59 (s, 5H, Cp); 5.52 (obscured by Cp, m, 1H, H_5); 5.21 (t, $J_{4\text{-}3/5}$ = 8.1 Hz, 1H, H_4); 2.95 (ddd, $J_{6\text{endo-}6\text{exo}}$ = 17.3, $J_{6\text{endo-}5}$ = 11.7 Hz, $J_{6\text{endo-}7\text{exo}}$ = 3.4 Hz, 1H, $H_{6\text{endo}}$); 2.50 (s, 3H, H_8); 2.15 (dddd, $J_{6\text{exo-}6\text{endo}}$ = 17.4 Hz, $J_{6\text{exo-}7\text{exo}}$ = 4.2 Hz, $J_{6\text{exo-}5}$ = 1.6 Hz, 1H, $H_{6\text{exo}}$); 1.75 (s, 3H, H_9); 0.97 (d, $J_{10\text{-}6\text{exo}}$= 6.8 Hz, 3H, H_{10}); 0.42 (ddd, $J_{7\text{exo-}6\text{exo}}$= 4.6 Hz, $J_{7\text{exo-}10}$= 6.9 Hz, 1H, $H_{7\text{exo}}$); GCOSY (500 MHz, acetone-d$_6$) δ 7.21 (H_3) ↔ 5.21 (H_4), 2.50 (H_8), 1.75 (H_9); 5.52 (H_5) ↔ 5.21 (H_4), 2.95 ($H_{6\text{endo}}$), 2.15 ($H_{6\text{exo}}$); 5.21 (H_4) ↔ 2.15 ($H_{6\text{exo}}$); 2.95 ($H_{6\text{endo}}$) ↔ 2.15 ($H_{6\text{exo}}$), 0.42 ($H_{7\text{exo}}$); 2.15 ($H_{6\text{exo}}$) ↔ 0.42 ($H_{7\text{exo}}$); 0.97 (H_{10}) ↔ 0.42 ($H_{7\text{exo}}$); ^{13}C

NMR (125.694 MHz, acetone-d_6): δ 111.51 (C_2), 110.52 (C_1), 99.30 (C_3), 91.07 (C_4), 89.39 (Cp), 84.20 (C_5), 50.56 (C_6), 37.00 (C_7), 23.53 (C_9), 20.53 (C_8), 16.06 (C_{10}); gHSQC (499.823 MHz, acetone-d_6): δ 99.30 (C_3) ↔ 7.21 (H_3); 91.07 (C_4) ↔ 5.21(H_4); 89.39 (Cp) ↔ 5.59 (Cp); 84.20 (C_5) ↔ 5.52 (H_5); 50.56 (C_6) ↔ 2.95 (H_{6endo}), 2.15 (H_{6exo}); 37.00 (C_7) ↔ 0.42 (H_7); 23.53 (C_9) ↔ 1.75 (H_9); 20.53 (C_8) ↔ 2.50 (H_8); 16.06 (C_{10}) ↔ 0.97 (H_{10}); gHMBC (499.823 MHz, acetone-d_6): δ 111.51 (C_2) ↔ *2.50 (H_8), 2.15 (H_{6exo});* 110.52 (C_1) ↔ *1.75 (H_9),* 0.97 (H_{10}); δ 99.30 (C_3) ↔ 2.50 (H_8); 91.07 (C_4) ↔ 2.95(H_{6endo}); 84.20 (C_5) ↔ 2.95(H_{6endo}); 50.56 (C_6) ↔ 5.21 (H_4), 1.75 (H_9), 0.97 (H_{10}), 0.42 (H_{6exo}); 37.00 (C_7) ↔ 5.52 (H_5), 2.95 (H_{6endo}), 1.75 (H_9), 0.97 (H_{10}); 20.53 (C_8) ↔ 7.21 (H_3). Anal. calcd for $C_{15}H_{20}CoBF_4$: C, 52.06, H, 5.83; Found: C, 51.8668; H, 5.8396. Electrospray MS *m/z* calculated for $C_{15}H_{20}Co$ (M^+), 259.08915; Found: 259.08897.



72 136 137

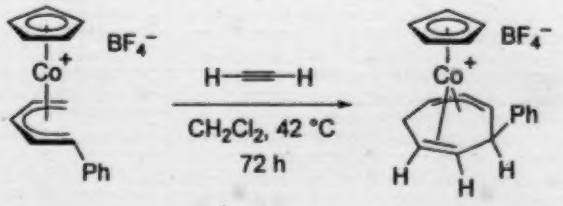
[CpCo(η^3,η^2-1-*endo*-methyl-3-trimethylsilylcycloheptadienyl)]$^+$BF$_4^-$ (136) and [CpCo(η^3,η^2-1-*endo*-methyl-2-trimethylsilylcycloheptadienyl)]$^+$BF$_4^-$ (137). A glass reaction bomb was charged with a solution of **72** (100 mg, 0.3425 mmol) in dichloromethane (~ 3 mL). An aliquot of trimethylsilylacetylene (33.64 mg , ~0.3425 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction (yield undetermined) was collected and, upon removal of solvent, was comprised of a slight majority (4 : 3) of the expected product **136** as compared with an unidentified compound (tentatively assigned as complex **137**). ^{1}H NMR (400 MHz, acetone-d_6): δ 5.70 (s, 5H, Cp), 5.30 (m, 1H, H_3), 4.63 (t, 1H, H_1), 4.15 (m, 1H, H_2), 3.61 (m, 1H, H_6), 3.12 (m, 1H, H_{4endo}), 2.58 (m, 1H, H_{7exo}), 2.20 (m, 1H, H_{4exo}), 1.60 (d, 3H, H_8), 0.38 (s, 9H, H_9).



72 **134** **135**

[CpCo(η^3,η^2-1-*endo*-methyl-2-ethoxycycloheptadienyl)]$^+$BF$_4^-$ (134) and [CpCo(η^3,η^2-1-*endo*-methyl-3-ethoxycycloheptadienyl)]$^+$BF$_4^-$ (135). A glass reaction bomb was charged with a solution of **72** (100.0 mg, 0.3425 mmol) in dichloromethane (~ 3 mL). An aliquot of ethoxyacetylene (24.0 mg, 3.425 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at room temperature for 30 min. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction (yield undetermined) was collected and, upon removal of solvent, which was comprised of a 1 : 1 mixture of (tentatively assigned) regioisomers **134** and **135**. **Regioisomer 134**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.58 (td, 1H, H_3), 5.40 (s, 5H, Cp), 4.99 (dd, 1H, H_1), 4.12 (t, 1H, H_2), 3.77

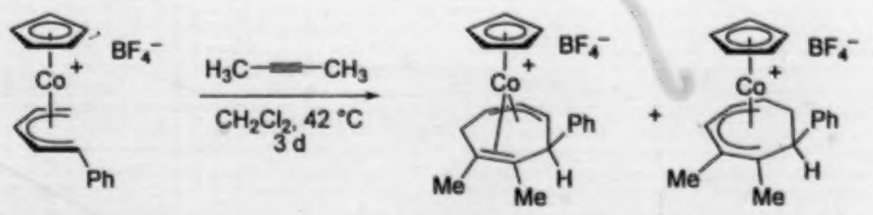
(dq, 2H, -OC$\underline{H}_2$CH$_3$), 3.50 (ddd, 1H, H$_5$ or H$_6$), 3.22 (dd, 1H, H$_{7exo}$), 3.18 (dd, 1H, H$_{4endo}$), 2.12 (d, 1H, H$_{4exo}$), 1.63 (d, 3H, H$_8$), 1.34 (overlap with isomer I methyl, td, 3H, -OCH$_2$C$\underline{H}_3$). **Regioisomer 135**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.30 (s, 5H, Cp), 5.04 (td, 1H, H$_3$), 4.69 (dd, 1H, H$_1$), 4.02 (t, 1H, H$_2$), 3.85 (q, 2H, -OC$\underline{H}_2$CH$_3$), 3.31 (dd, 1H, H$_5$ or H$_6$), 3.16 (dd, 1H, H$_{7exo}$), 3.13 (dd, 1H, H$_{4endo}$), 2.15 (d, 1H, H$_{4exo}$), 1.62 (d, 3H, H$_8$), 1.34 (td, 3H, -OCH$_2$C$\underline{H}_3$); **Isomeric mixture**: Electrospray MS *m/z* calculated for C$_{15}$H$_{20}$OCo (M$^+$), 275.08407; Found: 275.08416.



73 **140**

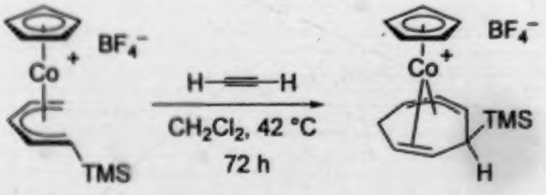
[CpCo(η^3,η^2-1-*endo*-phenylcycloheptadienyl)]$^+$BF$_4^-$ (140). Complex **73** (100 mg, 0.2825 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL) and placed in a reaction bomb. Simultaneously, acetylene was bubbled through CH$_2$Cl$_2$ in a test-tube for 20 minutes in order to ensure saturation. Then, ~2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at RT over 3.5 days. The solvent was then removed *in vacuo* and the product purified by silica gel chromatography using 3% MeOH/CH$_2$Cl$_2$. The red fraction was collected and dried providing 74.4 mg (69%) of total product as a dark, red powder. The ^{1}H NMR spectrum showed that there was a majority (ca. 83%) of starting complex **73** and ca. 17% of η^3,η^2-isomer **140**. IR (microscope, cm^{-1}): 3520 (br), 3119 (m), 3026 (w), 2928 (m), 1668 (m), 1643 (m), 1619 (m), 1494 (w), 1450 (w), 1417 (w), 1286 (w), 1054 (br s), 866 (m), 753 (m), 700 (m). ^{1}H

NMR (500 MHz, $CDCl_3$): δ 7.58 (m, 2H, Ph), 7.45 (m, 3H, Ph), 5.70 (s, 5H, Cp), 5.18 (ddd, 1H, H_1), 4.95 (dd, 1H, H_3), 4.15 (t, $J = 7$ Hz, 1H, H_2), 3.89 (ddd, 1H, H_6), 3.57 (dd, 1H, H_5), 3.44 (dd, 1H, H_{4endo}), 2.34 (dd, 1H, H_{7exo} or H_{4exo}), 1.60 (m, 1H, H_{4exo} or H_{7exo}); GCOSY (500 MHz, $CDCl_3$): δ 7.55 (Ph) ↔ 7.45 (Ph); 4.95 (H_3) ↔ 3.44 (H_{4endo}); 3.89 (H_6) ↔ 2.34 (H_{7exo}). Electrospray MS *m/z* calculated for $C_{18}H_{18}Co$ (M^+), 293.07350; Found: 293.07370.



73 **142** **143**

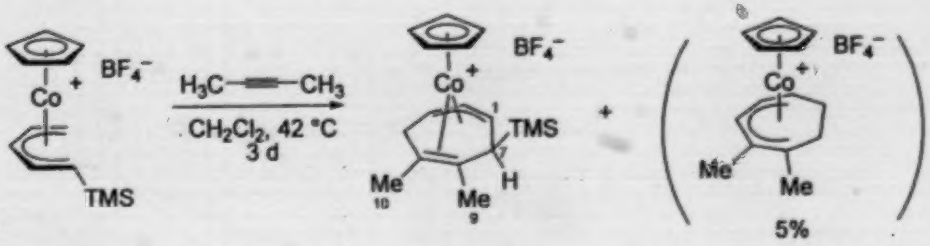
[CpCo(η^3,η^2-2,3- dimethyl-1-*endo*-phenylcycloheptadienyl)]$^+$$BF_4^-$ (142) and **[CpCo(η^5-2,3-dimethyl-1-*endo*-phenylcycloheptadienyl)]$^+$$BF_4^-$ (143).** A glass reaction bomb was charged with a solution of complex **73** (100 mg, 0.2825 mmol) in dichloromethane (~ 4 mL). The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, provided the product mixture, comprised primarily of the 72.4 mg (63%) of total product as a red oily residue. The ^{1}H NMR spectrum showed that this product mixture was a majority (ca. 87%) of η^3,η^2-isomer **142** and only a minor amount (ca. 13%) of fully conjugated η^5-isomer **143**. The sample was purified by recrystallization using pin-hole diffusion to provide an analytically pure sample of the mixture of isomers. **η^5-isomer**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7. 55 (d, 3H, Ph), 7.37 (t, 2H, Ph), 7.28 (m, 1H, H$_3$), 5.76 (m, 1H, H$_4$), 5.64 (s, 5H, Cp), 5.34 (m, 1H, H$_5$), 3.88 (m, 1H, H$_{6exo}$), 2.38 (m, 1H, H$_{6endo}$), 2.08 (s, 3H, H$_8$), 1.52 (m, 1H, H$_{7exo}$) 1.40 (s, 3H, H$_9$); GCOSY (500 MHz, CDCl$_3$): δ 7. 55 (d, 3H, Ph) ↔ 7.37 (t, 2H, Ph); 7.28 (m, 1H, H$_3$) ↔ 5.76 (m, 1H, H$_4$); 5.34 (m, 1H, H$_5$) ↔ 2.38 (m, 1H, H$_{6endo}$); 3.88 (m, 1H, H$_{6exo}$) ↔ 2.38 (m, 1H, H$_{6endo}$), 1.52 (m, 1H, H$_{7exo}$); 2.38 (m, 1H, H$_{6endo}$) ↔ 1.52 (m, 1H, H$_{7exo}$). **η^3,η^2-isomer**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.53 (m, 2H, Ph), 7.48 (m, 3H, Ph), 5.43 (ddd, 1H, H$_3$), 5.38 (s, 5H, Cp), 4.25 (t, 1H, H$_2$), 3.67 (dd, 1H, H$_1$), 3.24 (dd, 1H, H$_{4endo}$), 2.74 (dd, 1H, H$_{4exo}$), 2.38 (m, 1H, H$_{7exo}$), 2.06 (s, 3H, H$_8$), 1.39 (s, 3H, H$_9$); ^{1}H NMR (400 MHz, acetone-d$_6$): δ Ph, Ph, Cp, 5.44 (m, 1H, H$_3$), 4.32 (td, 1H, H$_2$), 3.81 (ddd, 1H, H$_1$), 3.27 (dd, 1H, H$_{4endo}$), 2.94 (dd, 1H, H$_{4exo}$), 1.78 (m, 1H, H$_{7exo}$); GCOSY (400 MHz, CDCl$_3$): δ 7.53 (Ph) ↔ 7.48 (Ph); 5.43 (H$_3$) ↔ 4.25 (H$_2$), 3.67 (H$_1$), 3.24 (H$_{4endo}$), 2.74 (H$_{4exo}$); 3.67 (H$_1$) ↔ 2.38 (H$_{7exo}$); 3.24 (H$_{4endo}$) ↔ 2.74 (H$_{4exo}$). Anal. calcd for $C_{15}H_{17}CoBF_4$: C, 58.86; H, 5.43; Found, C, 59.1655; H, 5.5673. Electrospray MS *m/z* calculated for $C_{20}H_{22}Co$ (M$^+$), 321.10507; Found: 321.10480.



74 **144**

[CpCo(η^3,η^2-1-*endo*-trimethylsilylcyclohepta-2,5-dien-1-yl)][BF$_4$] (144). Pentadienyl complex **74** (100 mg, 0.2856 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL) and placed in a reaction bomb. Simultaneously, acetylene was bubbled through CH$_2$Cl$_2$ in a test-tube for

20 minutes in order to ensure saturation. Then, ~2 mL of this saturated solution was transferred to the bomb via cannula. The bomb was sealed and allowed to stand at 40 °C over 3 days. The solvent was then removed *in vacuo* and the product purified by silica gel chromatography using 3% MeOH/CH_2Cl_2. The red fraction was collected and dried, providing 115.3 mg (94%) of η^3,η^2-isomer **144** as a dark, red powder. ^{1}H NMR (400 MHz, acetone-d_6): δ 5.05 (m, 1H, H_3), 4.95 (m, 1H, H_1), 4.10 (m, 1H, H_2), 3.90 (m, 1H, H_5), 3.62 (m, 1H, H_6), 3.10 (m, 1H, H_{4endo}), 2.40 (m, 1H, H_{4exo}), 1.88 (m, 1H, H_{7exo}); GCOSY (400 MHz, acetone-d_6): δ 5.05 (H_3) ↔ 4.10 (H_2), 3.10 (H_{4endo}), 2.40 (H_{4exo}); 4.95 (H_1) ↔ 4.10 (H_2), 1.88 (H_{7exo}); 3.90 (H_5) ↔ 3.62 (H_6), 3.10 (H_{4endo}); 3.62 (H_6) ↔ 1.88 (H_{7exo}); 3.10 (H_{4endo}) ↔ 2.40 (H_{4exo}). Electrospray MS *m/z* calculated for $C_{15}H_{22}CoSi$ (M^+), 289.08173, Found: 289.08147.



74 **146** **129**

[CpCo(η^3,η^2–2,3-dimethyl-1-*endo*-trimethylsilylcyclohepta-2,5-dien-1-yl)][BF_4] (146). A glass reaction bomb was charged with a solution of **74** (100 mg, 0.2856 mmol) in dichloromethane (~ 3 mL). An aliquot of 2-butyne (224 µL, ~2.856 mmol) was injected via syringe. The bomb was sealed, and the solution was maintained at 42 °C for 72 h. The solvent was removed *in vacuo* and the red residue was chromatographed on silica gel with a 3% methanol/dichloromethane eluent. The deep red fraction was collected and, upon removal of solvent, was a powder that was identified as complex **146** with a trace (~5% by NMR spectroscopy) of the desilylated fully conjugated product **129**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.43 (ddd, 1H, H_3), 5.37 (s, 5H, Cp), 5.05 (dd, *J* = 5.9, *J* = 6.8 Hz, 1H, H_1), 4.29 (dd, *J* = 6.1, *J* = 7.1 Hz, 1H, H_2), 3.18 (dd, *J* = 9.5 Hz, *J* = 14.2 Hz, 1H, H_{4exo}), 2.68 (dd, *J* = 3.4 Hz, *J* = 14.4 Hz, 1H, H_{4endo}), 2.10 (s, 3H, H_{10Me}), 2.02 (s, 3H, H_{9Me}), 1.90 (d, *J* = 5.9 Hz, 1H, H_{7exo}), 0.40 (s, 9H, C_{8TMSMe}); GCOSY (300 MHz, $CDCl_3$): 5.43 (H_3) ↔ 4.29 (H_2), 3.18 (H_{4exo}), 2.68 (H_{4endo}); 5.05 (H_1) ↔ 4.29 (H_2), 1.90 (H_{7exo}); 3.18 (H_{4exo}) ↔ 2.68 (H_{4endo}); ^{13}C NMR (125.694 MHz, $CDCl_3$): δ 88.88 (C_2), 88.09 (Cp), 62.22 (C_5), 61.29 (C_6), 44.43 (C_3), 40.84 (C_1), 31.50 (C_4), 28.12 (C_7), 22.85 (C_9), 21. 22 (C_{10}), -1.76 (C_8). Electrospray MS *m/z* calculated for $C_{17}H_{28}CoSi$ (M^+), 317.11298; Found: 317.11303.